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The Commissioner of Patents and Trademarks
Washington, D.C. 20231
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Sir:

Re: New United States Continuation in Part Patent Application
       Inventor(s):   Garver et al.
       Title: DETERMINATION OF THE PROPERTY OF A SOLUTION OR SOLID
                       USING RAMAN RATIOS
       Our File: 51-6 US CIP

This is a Request for filing of a new CIP patent application of U.S. Serial No: **08/814,519 filed March 10, 1997** in the United States. Enclosed are

1.   Declaration signed by the Inventor(s);
2.   **54** pages of specification, **42** claims,**8** being independent; Abstract of the Disclosure;
3.   Formal drawings including **24** figures;
4.   A cheque in the amount of **$1476.00** to cover the filing fee.

Convention priority is claimed under 35 USC 119 with respect to U.S. Patent Appln. No: **05/814,519** filed **March 10, 1997.**

We will be pleased to receive the filing particulars of this application.

Please charge any additional fees or credit overpayment to Deposit Account No: 20-0345.

Respectfully submitted,

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Determination of the Properties of a Solution or Solid Using Raman Ratios

This application is a continuation in part of US Patent Application Serial No. 08/814,519 filed on March 10, 1997.

5

Field of the Invention

This invention relates to an apparatus and a method for analyzing properties of a solution or solid using Raman spectroscopy and in particular to the application of Raman peak intensity
10   ratios for analyzing and predicting the properties of a solution or solid.

Background of the Invention

In many industrial chemical processes, the amount of reactants, or input components, that
15   are used is less than or more than the amount necessary to carry the reaction to the point of obtaining a desired characteristic(s) of the product stream. If too little of the input component is used, often the desired target value of a characteristic from the process is not obtained. Alternatively, if an excessive amount of an input component is used, the desired characteristic may be obtained, but the excess input component is typically
20   released as waste in the effluent of the process. In other cases, excessive amounts of an input component may cause undesirable reactions to occur that produce unwanted characteristics. Further, the wasted input component is economically costly and can become an environmental pollutant if it is released into the environment without being removed or recycled from the effluent. The difficulty in controlling chemical processes,
25   such as bleaching, in the pulp and paper manufacturing industry can be caused by a number of factors including qualitative and quantitative variability of the pulp or wood furnish, the composition of the process chemicals, and the consistency (% wood or pulp) of the furnish. Further, changing market requirements for paper products may require a paper manufacturing operation to produce a wide variety of paper grades. New paper

processing methods, equipment, and chemicals force the paper bleaching operation to adapt to these technical changes while still monitoring various characteristics of the pulp.

5   It is therefore desirable to be able to precisely control the input components to obtain the desired target characteristic(s) with little waste. To obtain this control, a characteristic of the effluent of an industrial process should be precisely monitored in real time in order to provide feedback control on the amount of input components which should be added to the reactor to avoid under use or excessive use, and waste, of the input component.

10   For example, in the pulp and paper industry, hydrogen peroxide and the hydroperoxy anion (HO_2^-) are important input components for the oxidation and bleaching of wood pulps. In a typical pulp bleaching plant situation, the control of the bleaching chemicals is based on the brightness of the incoming pulp, the pulp flow, and the target brightness and pulp physical properties that are to be achieved. The factors of incoming pulp
15   brightness, pulp flow, and target brightness are then used to calculate the amount of bleaching chemicals required to be added to the pulp to achieve a certain final target brightness. In another system, the brightness of the pulp is measured after bleaching chemicals are added and after allowing the reaction to occur for a defined reaction time. The resultant brightness value of the reaction is then measured and is used for feedback
20   regulation of the bleaching chemicals.

       Typically with these feedback systems, the amount of hydrogen peroxide that is used exceeds or overshoots the amount necessary to reach a final target characteristic, such as pulp final target brightness, yellowness, residual peroxide, brightness efficiency,
25   yellowness efficiency, and delignification efficiency. The resultant unwanted variation in these pulp characteristics may cause additional processing problems in the pulp and paper processing mill. Further, in the case of peroxide bleaching, excessive use of hydrogen peroxide results in waste hydrogen peroxide in the pulp effluent, which is both costly and environmentally harmful.

30

In order to solve these problems the prior art has offered various solutions. For example, United States Patent No. 4,878,998 teaches a method for bleaching of mechanical, thermomechanical and chemi-mechanical pulps whereby peroxide bleaching is controlled by the addition of a preset amount of bleaching chemicals at a first bleaching stage,

5   measuring the brightness of the pulp, feed forwardly adjusting the amount of bleaching chemicals to be added at a second bleaching stage as a function of the measured brightness of the pulp from the first stage, and then bleaching the pulp at the second stage.

10   Canadian Patent No. 2,081,907 teaches a method and apparatus for determining information characteristics of the concentration of each of at least three intermixed components in kraft liquors having the steps of: identifying detectable characteristics that are detectable in relation to the concentration of the components, developing a mathematical relationship between the component and the characteristics, such as

15   regression analysis, analysing a sample of solution with a UV detector, and then controlling the concentration of each of the three components by using the information from the analysis of the sample.

While current brightness sensors are able to provide a measure of the pulp brightness,

20   they are unable to measure the bleaching efficiency of the bleaching reaction itself. Bleaching efficiency is a change in brightness of a pulp divided by the amount of peroxide consumed during the bleaching reactions. Further, measurement of yellowness efficiency, which is defined as a change in pulp yellowness divided by the peroxide consumed during the bleaching reactions, also requires a method by which the residual

25   peroxide in the pulp effluent can be measured. Other efficiency measures relating the relative improvement in pulp optical and strength properties to the consumption of chemicals and the generation of dissolved species derived from wood are of interest, but are not readily available.

United States Patent No. 5,842,150 and WO 96/122183 to Renberg et al. disclose a
method, based on UV/VIS/NIR/IR, for the qualitative and quantitative determination of
quality parameters in pulp and paper and/or the organic content in effluents from pulp and
paper production by applying chemometric methods. Renberg et al. provide a review and

5   discussion of the "state of the art" and the need for on-line measurement of variables
related to pulp and effluent quality. A discussion is provided for the use of spectral
analysis with standard chemometric procedures to derive calibrated values for pulp and
paper strength and brightness parameters and also measures of amounts of organic
substances, for example the Total Organic Carbon (TOC), the Chemical Oxygen Demand

10   (COD), and the Biological Oxygen Demand (BOD). The abstract and the disclosure
indicate that the invention relates to UV/VIS/NIR spectroscopy, including Raman
spectroscopy. However, the disclosure does not provide any examples or further
disclosure with respect to the use of Raman spectroscopy. The examples disclosed in
column 7 in United States Patent No. 5,842,150 are all examples related to UV absorption

15   techniques between 200 and 360 nm to some other property. It is noted that United States
Patent No. 5,842,150 does not disclose any wavelength region outside the UV region.
Furthermore, Raman spectroscopy is an emission technique and does not extend to
absorption, transmittance or reflectance techniques as discussed in United States Patent
No. 5,842,150. The reflectance technique disclosed therein is not the same as an

20   emission by inelastic scattering as it occurs in Raman spectroscopy. The prior art does
not relate the spectral parameters to organic indicators and does not discuss the properties
related to the oxidative capacity of inorganic components that may exist in multiple
oxidation states, the development of substances that contribute to scale deposition of
effluent components, the physical properties of polymerizable species, such as the

25   number of endgroups, the extent of network formation, and the chain length, or the
development of bulk, yield or fiber flexibility.

The following two references, including references within, provide a general review of
the application and interpretation of Raman spectroscopy with respect to lignocellulosics,

30   Chapter 9 "An Overview of Raman Spectroscopy as Applied to Lignocellulosic

Materials" by Umesh P. Agarwal from a book entitled "Advances in Lignocellulosics Characterization", edited by Dimitris S. Argyropoulos, published by Tappi Press 1999 (ISBN 0-89852-357-5), and an article by Umesh P. Agarwal and Sally A. Ralph in Applied Spectroscopy Volume 51, Number 11, 1997. pp 1648-1655, entitled "FT Raman
5   Spectroscopy of Wood: Identifying Contributions of Lignin and Carbohydrate Polymers in the Spectrum of Black Spruce (Picea Mariana).

Unfortunately, it is well known that there is a present lack of an appropriate method or device for the monitoring and control of pulp bleaching reaction characteristics, including
10   pulp final target brightness, yellowness, residual peroxide, and efficiency, with respect to brightness or physical strength development, the amount of peroxide consumed, or the loss of lignin or carbohydrate substances. Also, it is known that pH measurement probes and electrochemical methods of measuring hydrogen peroxide, such as the Kajaani Polarox sensor made by Valmet Automation, can be unreliable under pH and chemical
15   concentration conditions which are typically used for pulp brightening reactions. BTG Spectris (Sweden) has an instrument and method of measuring the peroxide concentration that employs the use of a catalyst to decompose the hydrogen peroxide to generate oxygen gas that increases the reaction vessel pressure. This instrument, the RPA-5000, then relates the change in the pressure of the reaction vessel to the concentration of
20   peroxide. This method, while providing a badly needed measure of the peroxide concentration, is complicated and indirect and subject to variability related to sample preparation and instrument maintenance.

Measurement of the concentrations of other pulp bleaching chemicals such as sodium
25   hydrosulfite (dithionite), chlorine dioxide, and hypochlorite present similar difficulties to those encountered to for hydrogen peroxide. In general these bleaching compounds are oxidative or reductive substances, normally existing as one or more species of inorganic oxianions in solution. A review of the current state of the art of pulp bleaching practices, including methods for measurement and control, has been published (Pulp Bleaching.

Principles and Practice. Carlton W. Dence, and Duglas W. Reeve Editors. Tappi Press, Atlanta 1996).

5   **Summary of the Invention**

In accordance with the invention there is provided a method for measuring an amount of peroxide or peroxyl ion of a sample comprising the following steps: (a) irradiating at least a portion of the sample with a laser light for generating a Raman spectrum of the sample;

10   (b) obtain a Raman spectrum for obtaining at least two measurements at two different wavenumbers, a first measurement related to a Raman intensity related to an amount of peroxide or an amount of peroxyl ion, the second measurement related to the other of the amount of hydrogen peroxide and the amount of peroxyl ion; and (c) formulating a relationship between a Raman intensity for hydrogen peroxide and a Raman intensity for

15   the peroxyl ion by comparing information related to the two measurements for determing the amount of peroxide or peroxyl ion.

In accordance with another embodiment of the invention there is provided a method for determining a property of a sample comprising the steps of: (a) irradiating at least a

20   portion of the sample with a laser light for generating a Raman emitted light from the sample; (b) obtaining at least two measurements of the Raman emitted light between 200 cm^{-1} and 4000 cm^{-1}, a first measurement at a first wavenumber and a second measurement at a second wavenumber; and (c) determining a non-linear relationship between the at least two measurements and the property of the sample.

25

Furthermore, in accordance with yet another embodiment of the present invention there is provided a method for determining a potential of an oxidative reductive process comprising the following steps: (a) irradiating at least a portion of the sample with a laser light for generating a Raman emitted light from the sample; (b) obtaining at least two

30   measurements of the Raman emitted light between 200 cm^{-1} and 4000 cm^{-1}, a first

measurement at a first wavenumber, and a second measurement at a second wavenumber; and (c) determining a relationship between the two measurements and the potential of the oxidative reductive process. The term peak refers herein after to a maximum intensity value or a region about the maximum intensity, near or about the peak.

5

In accordance with the invention there is further provided a method for measuring an amount of at least one of hydrogen peroxide and peroxyl ion (HOO^-) in a solution, comprising the steps of: irradiating at least a portion of the solution with light of a suitable wavelength and intensity to obtain information relating to a Raman spectrum

10   thereof, said information containing data related to at least one of an intensity peak corresponding to peroxide and an intensity peak corresponding to peroxyl ion; and, processing the information to determine indicia of a concentration of at least one of hydrogen peroxide and peroxyl ion, the processing including an analysis of at least one of data related to the intensity peak corresponding to peroxide, data related to the intensity

15   peak corresponding to peroxyl ion, a sum of data related to the intensity peaks of the peroxide and peroxyl ion, a product of data related to the intensity peaks of the peroxide and peroxyl ion, and a ratio of data related to the intensity peaks of the peroxide and peroxyl ion.

20   In accordance with a further embodiment of the present invention there is provided an apparatus for determining a property of a sample comprising: a laser light source for irradiating at least a portion of the sample for generating a Raman emitted light from the sample; a detector for detecting the Raman emitted light from the sample, said detector for obtaining at least two measurements of he Raman emitted light, a first measurement at

25   a first wavenumber and a second measurement at a second wavenumber; and a processor for receiving and processing data from the detector for determining a non-linear relationship between the at least two measurements and the property of the sample.

In accordance with another aspect of the invention there is provided a system for

30   determining a property of a sample comprising: means for determining a non-linear

relationship between at least two measurements and the property of the sample, the at least two measurements corresponding to Raman emitted light between 200 cm^{-1} and 4000 cm^{-1}, and the at least two measurements comprising a first measurement at a first wavenumber and a second measurement at a second wavenumber.

5

Further more, in accordance with the invention there is provided a system for determining a property of a sample comprising: means for comparing at least two measurements including a first measurement at a first wavenumber and a second measurement at a second wavenumber, the at least two measurements corresponding to Raman emitted light between 200 cm^{-1} and 4000 cm^{-1} when the sample is irradiated with a laser; means for determining a non-linear relationship between the at least two measurements and the property of the sample; and, means for determining the property of the sample in dependence upon the non-linear relationship.

15   In accordance with a further aspect of the invention there is provided a system for determining an amount of at least one of hydrogen peroxide and HOO- in a solution, comprising: means for receiving information containing data related to at least one of a Raman intensity peak corresponding to peroxide and a Raman intensity peak corresponding to peroxyl ion; and, means for processing the information to determine

20   indicia of a concentration of at least one of peroxide and peroxyl ion, the processing including an analysis of at least one of data related to the intensity peak corresponding to peroxide, data related the intensity peak corresponding to peroxyl ion, a sum of data related to the intensity peaks of the peroxide and peroxyl ion, a product of data related to the intensity peaks of the peroxide and peroxyl ion, and a ratio of data related to the

25   intensity peaks of the peroxide and peroxyl ion.

Brief Description of the Drawings

30   Exemplary embodiments of the invention will now be described in accordance with the

drawings in which:

Figure 1 presents a schematic diagram of a pulp bleaching process in accordance with an embodiment of the present invention;

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Figure 2 shows a matrix plot for an example of a bleaching process and shows five dependent properties and six corresponding UV absorbance values;

Figure 3 shows a similar matrix plot, which was formed using the same characteristic properties and a representative set of ratios from the absorbance values;

10

Figure 4 presents an example from pulp and paper process waters and shows a plurality of absorbance spectra obtained at different temperatures between 20 and 80 degrees Celsius;

15

Figure 5 shows a matrix plot with one dependent property, viz. the temperature, and 6 corresponding UV-visible absorbance values;

Figure 6 shows a matrix plot with one dependent property, viz. the temperature, and a representative set of ratios from the absorbance values;

20

Figure 7 shows a plot presenting Raman spectra from a dispersive system with a 514.5 nm laser and a FT system with a 1064 nm laser;

25   Figure 8 shows a Fourier Transform (FT) scan of a Raman scattering signal from a pulp bleaching mixture of hydrogen peroxide, silicate, and sulfate;

Figure 9 shows a series of Raman spectra of pressates from peroxide bleaching of pulp;

Figure 10 shows a matrix plot for variables related to Aspen TMP pulp bleaching with hydrogen peroxide, Raman intensities, Raman intensity ratios and the pulp and bleaching pressate properties;

5   Figure 11 presents Raman Spectra of pressates from hydrogen peroxide bleaching of aspen TMP pulp at different pH values;

Figure 12 shows a graph for the prediction of pulp brightness from a model based on a combination of Raman peak intensities and Raman peak intensity ratios;

10
Figure 13 resents the Raman spectra showing HOO⁻ and HOOH peaks at 850 cm⁻¹ and 877 cm⁻¹ , respectively;

Figure 14 shows a matrix plot of Raman intensities and Raman ratios as a function of pH;

15
Figures 15 and 16 show Raman spectra of different sulfur oxianion in a dibasic form;

Figure 17 presents spectra showing Raman intensities of a solution of sodium hydrosulfite $(Na_2S_2O_4)$ oxidizing to sulfate and sulfite ions;

20
Figure 18 shows the S-O stretching region of the Raman spectrum during the oxidation of hydrosulfite to sulfate;

Figure 19 presents a matrix plot showing Raman intensities, and Raman intensity ratios with

25   time and oxidation reduction potential (ORP);

Figure 20 presents a series of silicate Raman spectra as a function of varying hydroxide concentration as taken from Prabir K. Dutta and Dah-Chung Shieh, published in Applied Spectroscopy, Vol. 39, No. 2, pp. 343-346 (1985);

30

Figure 21 shows the intensities of the different peaks as derived from the spectra presented in Figure 20;

Figure 22 showing a matrix plot of Raman intensity ratios as a function of the HO^-/Si ratio;

5

Figure 23 shows Raman spectra of white water samples from ANC and MWP; and

Figure 24 shows Raman spectra of Acetic acid and Acetic acetate buffer solution. Top line: 0.05M acetic acetate buffer solution. Bottom line: 5% acetic acid solution (scaling X 0.2).

10

Detailed Description of the Invention

Figure 1 presents a schematic diagram of a pulp bleaching process in accordance with an
15   embodiment of the present invention. As shown in Figure 1, wood pulp 2 is bleached in a bleaching chamber 4, by bleaching agent hydrogen peroxide (H_2O_2), as input component. H_2O_2 flows from reservoir 18 through control valve 16 into the bleaching chamber 4. The output of the bleaching process is a process effluent 6, which includes both the bleached pulp as well as the bleaching liquor.

20

A sample of the effluent 6 is diverted to a Raman spectrometer 10 for the purpose of obtaining at least two measurements of UV light absorption of the effluent 6 and then calculating the ratio of the two measurements. The ratio of the Raman emitted light intensity measurements have been found to correlate to various characteristics of the pulp
25   effluent. For example, characteristics such as pulp brightness, pH, and pulp yellowness, and residual peroxide can be determined through the use of different Raman wavenumbers in the ratio.

The bleaching process causes structural changes in the lignin or extractive components of
30   the pulp including ionization of the phenolic groups of the lignin molecule. Lignin

degradation typically results in an increase in the number of phenolic groups that can be ionized by changes in pH. As a result, the relative amount of ionized phenolic groups usually depends on the extent of lignin degradation and pH.

5   In accordance with an embodiment of the present invention, the effluent 6 is filtered by a 0.05 µm cross-flow membrane filter (Koch Filtration #5-HMF-451 PNE-PP) filter to remove colloidal material from the pulp effluent. If the colloidal material is not removed from the effluent, the resultant turbidity may interfere and offset the Raman intensities and hence affect the Raman ratio of the present invention.

10

Computer 12 calculates a mathematical relationship between two or more Raman measurements, which is a ratio or combination of ratios in this embodiment of the present invention. Moreover, computer 12 stores in its memory a predetermined value for a characteristic of the effluent.

15

Appropriate software provides means for receiving information pertaining to the Raman measurements and means for processing this information. The processing of the information includes the comparison of measurements, the determination of non-linear relationships, and the determination of a property or properties of the sample.

20

Computer 12 acts as a comparing means for comparing the measured H_2O_2 value with a predetermined H_2O_2 value. This comparison step determines the actual empirical value of the residual weight percentage of H_2O_2, a characteristic of the effluent being monitored.

25   According to this embodiment, computer 12 determines whether to send a feedback signal 14 to control valve 16 to adjust the amount of H_2O_2 being fed into the bleaching process taking place in bleaching chamber 4. Thus, computer 12 together with control valve 16 acts as a means for adjusting the amount of input component, such as H_2O_2, according to the value of the characteristic of the effluent 6, H_2O_2 concentration, which

30   was determined by the ratio of the Raman emitted light measurements.

Thus, as shown in the embodiment of the invention, shown in Figure 1, the disclosed invention permits a real time feedback control of a pulp bleaching process. The feedback system provides sufficient H_2O_2 to the pulp bleaching process without producing

5   excessive waste residual H_2O_2 or pollution.

If desired, other input components, such as NaOH, $MgSO_4$, or a chelating agent, such as DTPA (diethylenetriamine pentaacetic acid), are added to the bleaching reaction in reduced or increased amounts in accordance this feedback system.

10

Richardson et al. disclose in U.S. Patent No. 5,242, 602 a method for simultaneously analyzing the concentration of performance indicators in aqueous systems by determining an absorbance or emission spectrum in a wavelength range from 200 to 2500 nm and applying chemometric algorithms to the absorbance or emission spectrum. The

15   concentrations of the performance indicators determined by the chemometric algorithms are compared to predefined ranges for the respective performance indicators. Thus, this technique teaches the application of chemometrical methods for multicomponent analysis using multiwavelength spectroscopy. Richardson et al. describe the following four basic algorithms to extract and analyze features in the overall absorption or emission spectra

20   that are specific to the qualitative and quantitative contributions from the specific performance indicators:

       1. *Quantification.* Measurement of the absorption or emission spectra on a series of samples with known concentrations of the performance indicators.

25   2. *Processing.* The processing of raw data to reduce noise and optimize the ability of the chemometric techniques to compare known spectra with unknown spectra or to act on specific features for the spectra of a multi-components solution to permit analysis of multi-components solutions or to adjust for noise or drift. The following preprocessing steps were explicitly identified: a) noise reduction or smoothing; b) Fourier

30   or Walsh transformations; c) first or second derivatives; and d)correction for drift.

3. *Analysis.* Analysis of the spectra using chemometric techniques. The following statistical methods were specifically identified: a) principal component analysis; b) regression analysis including multiple regression methods; and c) discriminant analysis.

4. *Comparison.* Comparison of results from the analysis to actual values. This

5   step may involve the use of multiple linear regression on 2-4 Principal components to obtain a calibration for different performance indicators.

In the method disclosed by Richardson et al. the chemometric algorithms are applied directly to the absorbance or emission spectrum. However, the *Analysis* methods

10   described in U.S. Patent No. 5,242,602 are ineffective if there is a small variation or a high degree of correlation in the data matrix. The present invention discloses the use of a ratio or multiple ratios from the at least two measurements for computing an empirical value of the characteristic. This is a significant improvement from the method described by Richardson et al. in that the present invention can extract the variation even if the

15   obtained absorbance or emission spectra are similar, i.e. they show little variation. The method disclosed by Richardson et al. does not provide any mention in the processing step for the use of ratios as a means to improve the analysis step. Furthermore, there is no specific mention of using ratios as a means of reducing the redundancy of the data that may lead to analysis problems. The invention disclosed by Richardson et al. does not

20   address problems related to the reliability of the estimation of a property/characteristic that has a small variation relative to the total variation in the data.

The present invention discloses the use of at least one ratio and a value formulated from at least two Raman measurements, each at different wavenumber, to determine a

25   characteristic of a process effluent. Combinations of the disclosed ratios may be further used to monitor and control characteristics of the process effluent. Multiple regression analysis, using a forward stepwise multiple regression, was conducted using these Raman ratios to determine the best combination of these ratios and coefficients, (i.e. a predetermined relationship) which best predicted the final property of the pulp (i.e.

30   optical properties and other descriptors of bleaching including delignification efficiency

and residual peroxide). As shown in the graphs, the present invention can use this predetermined relationship to determine a pulp property (final brightness, delignification efficiency, or residual peroxide) using a minimum number of Raman ratio measurements.

5   A more detailed description of the problems associated with the extraction of multiple properties from a series of similar ultraviolet-visible spectra is given below. The use of ratios formulated from Raman measurements provides a means for accentuating the difference between the obtained spectra. A description of the problems with the extraction of multiple properties from a series of similar Raman spectra. The method

10   disclosed by Richardson et al. could not be used to separate the variables or parameters since they often cause the same kind of changes in the spectra or the absolute changes are relatively small. The present invention makes use of relative changes to control the number of parameters.

15   The analysis methods, such as Principal Component Analysis, Regression Analysis, and Discriminant Analysis, described by Richardson et al. relate linear combinations of measured variables with the observable characteristic. The instant invention relates at least one ratio and a value to a characteristic of pulp or the process effluent and implicitly accommodates nonlinear relationships between the measured values and the determined

20   characteristic. Strictly speaking a chemical concentration should be linear with the absorbance or emission at different wavelengths. One object of the present invention is to obtain a relationship between a set of emission values and a characteristic that is a complicated nonlinear function of a plurality of different chemical and physical factors, such as the delignification efficiency. However, there are many problems with applying

25   statistical analysis directly to a series of similar Raman spectra that are described below. Ultimately, the best result is only as good as the inherent variance in the data. Analysis using a set of absorbance or emission ratios alone or in combination with Raman emission or scattering values amounts to generating a new or expanded data set that has a greater variance than the original data set. A new data set will generate more accurate

30   and stable solutions if it contains arrays that relate more closely to the characteristic to be

15

fit than the original data. Analysis using a set of absorbance or emission ratios amounts to generating a new data set, based on functions from the initial data set, that is used with the chemometric techniques.

5   The statistical methods described by Richardson et al. require that the variation of the measured absorbance at different wavelengths changes substantially as a function of the different properties that are mathematically related to the absorbance values. Thus, small variation in the data matrix will result in computational difficulties in multiple-linear regression analysis. Further, a small variation in the relationships between variables, as

10   expressed in the correlation matrix, will result in additional computational difficulties in the principle component analysis. In this case, small relative variations may be easily masked by large absolute variations. The presence of small variations contributing to the response for different variables in the presence of large variations that are similar in the different variables results in an ill-conditioned or singular matrix of the absorbance values

15   that is not amenable to the statistical analysis described by Richardson et al. as discussed below in more detail using an exemplary data matrix.

The use of ratios obtained from ultraviolet-visible measurements can condition the data matrix to emphasize the variation of emission (or conversely absorbance) at one

20   wavelength to that of another. The analysis is then performed on the relative variation rather than on the absolute variation. If in the process to be monitored or controlled one substance is transformed into another, or if a small amount of one substance can have a substantial effect on the concentration of another, then the method of observing the relative changes is much more powerful than looking at absolute changes. The present

25   invention as defined in the claims uses at least one ratio and hence provides a means to selectively weigh the contributions from the at least two measurements, each at a different wavelengths.

The outstanding problems associated with the analysis of similar and featureless spectra

30   are well known and a discussion of those problems is described by O. Thomas and S.

Gallot. in Fresenius Journal for Analytical Chemistry, 1990, Volume 338, pages 234-237; and by B. Karlberg in the following PCT publication WO95/01560. The prior art does not provide any references to solve this problem by using a ratio. Despite numerous attempts to directly address the computational difficulties related to regression and

5   chemometrics with colinear data, there are no reports directly addressing the computational problem by using ratios.

In the case of the quantification or analysis methods described by Richardson et al., the data matrix would consist of a series of absorption or emission measurements on n

10   different samples (indexed by i) and p different wavelengths (indexed by j). For example:

Data Matrix in which the i index is the index for the sample and the j index is the index for the wavelength

15

$$\mathbf{A} = \begin{bmatrix} A_{1,1} & \cdots & A_{1,j} & \cdots & A_{1,p} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ A_{i,1} & \cdots & A_{i,j} & \cdots & A_{i,p} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ A_{n,1} & \cdots & A_{n,j} & \cdots & A_{n,p} \end{bmatrix}$$

In the statistical techniques described by Richardson et al., the sample correlation between variables is measured as a function of the variance (s_{ii}) and covariance (s_{ij}) of the

20   data. In this case i and j are two different indexes for the wavelength for the emission (or conversely absorbance) measurement and k is the index for n different samples.

$$r_{ij} = \frac{s_{ij}}{\sqrt{s_{ii} s_{jj}}}$$

$$s_{ii} = s_i^2 = \frac{1}{n-1} \sum_{k=1}^{n} (y_{k,i} - \bar{y}_i)^2$$

$$s_{ij} = \frac{1}{n-1} \sum_{k=1}^{n} (y_{k,i} - \bar{y}_i)(y_{k,j} - \bar{y}_j)$$

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From these calculations the sample covariance matrix **S** and correlation matrix **R** may be calculated.

5
$$\mathbf{S} = \begin{bmatrix} s_{11} & s_{12} & \cdots & s_{1p} \\ s_{21} & s_{22} & \cdots & s_{2p} \\ \vdots & \vdots & \ddots & \vdots \\ s_{p1} & s_{p2} & \cdots & s_{pp} \end{bmatrix}$$

$$\mathbf{R} = \begin{bmatrix} 1 & r_{12} & \cdots & r_{1p} \\ r_{21} & 1 & \cdots & r_{2p} \\ \vdots & \vdots & \ddots & \vdots \\ r_{p1} & r_{p2} & \cdots & 1 \end{bmatrix}$$

Multiple regression calculations require the calculation of the determinant of the data matrix **A**. The determinant of an n x n matrix is the sum of the products of the elements of a row of the matrix and their cofactors. A cofactor is a determinant of a matrix

10 obtained by eliminating the row and column of the element. Thus each cofactor may be obtained by calculating the products of elements of a row and the determinant of a matrix obtained by eliminating the row and column of each element. The calculation of the determinant has several important consequences:

15 1. Least squares multiple regression methods require calculation of the determinant of the data matrix to obtain a linear combination of the different variables. Colinear data, or a high degree of covariance, similarity or redundancy in the data matrix will lead to an ill-conditioned matrix that produces unstable results.

    a) If two rows or columns are nearly identical then the determinant will

20   be nearly zero.

    b) Solutions to a set of linear equations, for example as addressed when using multiple regression to obtain correlated physical properties from Raman spectra, depend on the division using the determinant of the matrix. Colinear variables are problematic in these types of

25   calculations. Therefore, the division by a very small number leads to instability in the calculation in cases where the determinant is near zero.

2.   In Principal Component Analysis (PCA) the colinearity problem is resolved by forming a new set of orthogonal variables, the principal components. The principal components are linear combinations of variables that express the maximum variance. The principal components may be used in a multiple regression technique to derive

5   relationships with properties related to the variables. The regression on principal component solves problems related to matrix singularity leading to problems with inversion. However, the number of principal components may be less than the number of variables and some valuable information may be lost in principal components that are considered statistically insignificant.

10   a) When the regression matrix **R** or the covariance matrix **S** is singular or ill-conditioned problems may occur in extracting principal components.

            b) If the relevant underlying effects are small in comparison with some irrelevant ones, then they may not appear among the first few principal

15   components. The resulting component selection problem is difficult as an arbitrary inclusion of the first n principal components may serve to degrade the performance of the model.

3.   Partial Least Squares (PLS) regression is a multivariate data analysis technique that can be used to extracts components (now called factors) that relate several response

20   (Y) variables to several explanatory (X) variables. The method aims to identify the underlying factors, or linear combination of the X variables, which best model the Y dependent variables. PLS can deal efficiently with data sets where there are very many variables that are highly correlated and involving substantial random noise.

            a) Richardson et al. in U.S. Patent No. 5,242,602 does not describe the use of

25   PLS although other descriptions of chemometrics describe the power of this technique in chemometric analysis.

            b) However, the partial least squares analysis is no better than the different linear functions that may be described from the data. If the property/characteristic that is to be predicted cannot be described as a

30   linear function of the variables x then the regression will introduce

systematic error into the regression model.

The analysis method described in accordance with the present invention amounts to generating a new data matrix that has the general appearance shown below.

5

Using a set of ratios the data matrix **A** is transformed into a new data matrix that may be called the ratio matrix **R**. This matrix is based upon a predetermined set of wavenumbers for the numerators and denominators of the ratios. The i index is the index for the sample and the j index is the index for the wavelength of the numerators, the k

10   index is the index for the set of wavelengths corresponding to the set of denominators that match the j indexed emission (or conversely absorbance) values for each sample. The ratio data matrix may be generally written as:

$$
\mathbf{R} =
\begin{bmatrix}
\dfrac{A_{1,1}}{A_{\lambda a_1}} & \cdots & \dfrac{A_{1,j}}{A_{\lambda k_1}} & \cdots & \dfrac{A_{1,p}}{A_{\lambda q_1}} \\[2ex]
\vdots & \ddots & \vdots & \ddots & \vdots \\[1ex]
\dfrac{A_{i,1}}{A_{\lambda a_i}} & \cdots & \dfrac{A_{i,j}}{A_{\lambda k_i}} & \cdots & \dfrac{A_{i,p}}{A_{\lambda q_i}} \\[2ex]
\vdots & \ddots & \vdots & \ddots & \vdots \\[1ex]
\dfrac{A_{n,1}}{A_{\lambda a_n}} & \cdots & \dfrac{A_{n,j}}{A_{\lambda k_n}} & \cdots & \dfrac{A_{n,p}}{A_{\lambda q_n}}
\end{bmatrix}
$$

15

The method disclosed by Richardson et al. in U.S. Patent No. 5,242,602 comprises the direct determination of an emission or absorbance spectrum. However, the method disclosed by Richardson et al. would not work with the present invention. For example, in order to control pulp bleaching processes it is necessary to separate the variables, i.e. it

20   is necessary to control a plurality of parameters. In peroxide bleaching processes, the pH and the amount of peroxide are the most important parameters to control. Nevertheless, to control those parameters it is not sufficient to look only at the levels of those two parameters. It is important to look at how the reaction has progressed which means it is necessary to extract a measure of how much peroxide is present, to extract a measure of

the pH, to extract a measure of how bright the pulp is, and to extract a measure of how

yellow the pulp is. Using the method taught by Richardson et al. it would not be possible

to extract these parameters because often these parameters cause generally the same kind

of changes in the measured spectra or alternatively the absolute changes in some

5   important areas of the spectrum are fairly small. In using the relative changes, i.e. ratios,

it is possible to extract the variables. For example, in peroxide bleaching processes there

are two main components to consider. One component is peroxide and the other

component is lignin. For the lignin component three aspects have to be considered: i)

How much lignin has been released from the pulp; ii) What is the intensity of the color of

10   the removed lignin components; and iii) what is the extent of lignin ionization? Thus to

optimize this reaction the peroxide and the amount of lignin removed is maximized under

the constraint of minimizing the color of the removed lignin. Pulp consists of about 30%

lignin which causes its yellow color and hence removing the lignin from the pulp makes

the pulp brighter. Lignin has a relatively broad diffuse spectrum and could be monitored

15   at almost any wavelength in the UV region. Since the bleaching process involves a

plurality of parameters this process cannot simply be optimized by maximizing the

amount of peroxide. The problem is that the competition between productive bleaching

reactions involving the nucleophilic peroxyl anion compete with destructive reactions

initiated by a (second order) bimolecular decomposition involving hydrogen peroxide and

20   the peroxyl anion. Variation in pH or peroxide concentrations yields a point where the

peroxide decomposition dominates over the productive bleaching reactions. Before that

point the improvements in the bleaching process are basically proportional to the pH or

the peroxide concentration until a maximum is reached in both. At the maximum the

peroxide decomposition leads to darkening reactions that neutralize the productive

25   bleaching reactions. Thus at this pH and this peroxide concentration the amount of

bleaching that has been done is no longer related to the amount of peroxide consumed

and also it is no longer related to the amount of lignin released. In fact, the trend is

opposite and has a non-linear equation. In the beginning, the amount of bleaching is

linear for a certain region when observing the bleaching versus the amount of peroxide

30   consumed or the bleaching versus the amount of lignin released. The bleaching is linear

in some regions but in fact it is a parabolic function and one observes a maximum. Using the method disclosed by Richardson et al., i.e. a linear function, it appears that the bleaching process is progressing but in reality this is not happening. Thus, it is necessary to identify when an unproductive loss in hydrogen peroxide and an unproductive

5 generation of the lignin occurs. This becomes important when the peroxide starts to decompose and superoxide and hydroxyl free radicals are formed. These free radicals start reacting with the lignin and large amounts of lignin are removed. However, the pulp whiteness decreases and increased amounts of peroxide are used without reaching optimum bleaching conditions or improving the brightness of the pulp. Therefore, it is

10 important that this point is characterized. The present invention discloses that when this point is approached, the color of the lignin changes with a resulting increase in the absorbance value at 350 nm, for example. The relative amount of color in the lignin increases substantially at that critical point. The method taught by Richardson et al. would detect this increase in absorbance as a result of lignin removal. Lignin has

15 intrinsic or natural color and when more lignin is removed more color is observed. This means, that in the initial bleaching stages lignin is removed with the intrinsic color. However, when the peroxide starts to break down, then a new kind of reaction occurs and more lignin is removed that is highly colored. Problems arise because at the same time these highly colored lignin species are generated on the pulp. The method by Richardson

20 et al. would measure changes in the amount of lignin removed but because this method does not make use of relative amounts it cannot distinguish between the desired removal of natural lignin and the undesired case where removal of highly colored lignin occurs as a result of a competing reaction when the peroxide breaks down. Thus without making use of absorbance or emission ratios it is not possible to obtain sufficient information to

25 distinguish between one reaction happening and another reaction happening. The method taught in U.S. Patent No. 5,242,602 can not manage this non-linear relationship.

The following example demonstrates the advantage of the present invention and how it addresses the critical point of extracting the variation by using ratios instead of applying

30 analysis techniques directly on the spectra or on the processed spectra as it was taught in

the method disclosed by Richardson et al. The presented example utilizes ratios obtained from UV absorbance measurements. This example is an example of a bleaching process and shows five dependent properties and six corresponding UV absorbance values. The absorbance values are representative, but are chosen to provide a large variance. Figure

5   2, shows a matrix plot for an example of a bleaching process and shows five dependent properties and six corresponding UV absorbance values. Each miniature plot in Figure 2 shows a bivariate plot of the corresponding diagonal elements. The variable on any given plot axis is determined by vertical and horizontal tracing to the variable at the plot diagonal, much like a mileage chart on a map. This matrix plot demonstrates that the

10   absorbance functions are highly colinear with each other. There are five different non-linear relationships between the absorbance values and the different properties: pH, residual H_2O_2, brightness, yellowness (indicated as BSTAR) and brightness efficiency. Furthermore, it is seen that there is scatter in the direct relationships between some of the characteristic properties and the absorbance values.

15

Figure 3 shows a similar matrix plot, which was formed using the same characteristic properties and a representative set of ratios from the absorbance values. Note that the colinearity between the ratio variables is much smaller than the colinearity between the absorbance values. Furthermore it is seen that the different UV-visible ratios vary

20   linearly with different properties. There is a high correlation coefficient between different single ratios and each of the characteristic properties. These correlation coefficients are given in Table 1 below.

Table 1

Property	UV ratio	Ratio Correlation	Wavelength UV absorbance	Single Linear Correlation
pH	A230/A250	-0.98	A250	0.96
H$_2$O$_2$ Residual	A230/A280	0.96	A280	-0.93
Pulp Brightness	A350/A250	-0.83	A400	-0.80
Yellowness (B*)	A350/A280	0.95	A400	0.95
Brightness Efficiency	A230/A400	0.52	A450	-0.42

Principle Component Analysis:

Using 9 UV values, only one factor may be extracted. This factor explains 97.6% of the

5   data variation. There is one other factor with an eigenvalue between 1.0 and 0.1.

However, using 9 UV ratios, two factors may be extracted. One factor explains 67.6% of

the data variation and the other explains 22.2% of the data variation. There are three

other factors with eigenvalues between 0.1 and 1.0.

10

The ability to extract more factors using principle component analysis indicates that the

data variation may be broken down into more independent factors using the ratio method.

Figure 4 presents an example from pulp and paper process waters. Figure 4 shows a

15   plurality of absorbance spectra obtained at different temperatures between 20 and 80

degrees Celsius. The small variation in the obtained spectra shows that there is a

chemical change as a function of the temperature. These formless spectra with their small

variations as a function of the process variable are typically encountered in the pulp and

paper industry as well as in many other industries consuming a large amount of process

20   water. Figures 5 and 6 present the matrix plots for this example. The set of spectra for

this example shows small variations in the absorbance values.

Figure 5 shows one dependent property, viz. the temperature, and 6 corresponding UV-visible absorbance values. In this case, one principle component accounts for 97% of the data variation. The general trend is for the absorbance values to decrease with increasing temperature. The principle components method can only resolve this effect, even though

5   it is clear that more is happening. A second principle component may be found if eigenvalues between 0.1 and 1.0 are allowed. This second eigenvalue accounts for only 2% of the variation.

Figure 6 shows one dependent property, viz. the temperature, and a representative set of

10   ratios from the absorbance values. In this case, two principle components account for 61.2% of the data variation and 27.6% of the data variation. A third principle component may be found if eigenvalues between 0.1 and 1.0 are allowed. Once rotated, the three eigenvalues may account for 40%, 34%, and 25% of the data variation.

15   In accordance with an embodiment of the present invention it is taught that an efficiency and ultimate extent of a mechanical pulp bleaching operation using hydrogen peroxide is monitored and controlled by analysis of the UV-visible spectrum or Raman spectrum of the pressate from the bleaching process. It was not previously known that the reactions on the components in the pressate were representative of the pulp bleaching process.

20   Bleaching control has always been done using pulp brightness and without observing the color of the pressate. Measurements of pulp brightness suffer from variability related to pulp consistency, pulp surface area or scattering and insensitivity. The present invention teaches that the amount of lignin in the pressate and the color of the pressate, as determined by UV ratios, reflected the bleaching progress during a mechanical pulp

25   bleaching process. Previously, these bleaching processes have been described only in terms of the reactions on the pulp and the reactions on the components in the pressate were thought to be trivial and different from the bleaching reactions. The method of using a series of ratios of absorbance or alternatively emission values from pressates has a further advantage because pressates are easier to analyze optically than the pulp. At the

30   point of maximum pulp brightness the response of pulp brightness is a flat function of

pulp bleaching variables such as pH and peroxide concentration. For this reason, pulp brightness is a very poor control parameter. Another unexpected and advantageous result is that a combination of UV ratios or Raman ratios provides sensitive measures at this point where traditional bleaching control sensors that monitor a pulp brightness fail. The

5   analysis disclosed in the patent describes that hydrogen peroxide bleaching of mechanical pulps can be controlled by monitoring a combination of the amount of hydrogen peroxide anion, the amount of lignin removed, and the relative amount of color removed during the bleaching process. Three points may be made concerning these parameters:

1. The removal of lignin was identified as an important process in the bleaching

10   of pulp. In the prior art this was not thought to be the case for mechanical pulps. However, excessive lignin removal can occur during inefficient bleaching processes that leads to a parallel increase in colored components. The best bleaching occurred when the most lignin could be removed while generating the smallest amount of colored components.

15   2. The bleaching process was most efficient when the relative amount of hydrogen peroxide anion was maintained at high levels. Underlying this simple statement are the realizations that the principle cause of inefficient bleaching is the degradation of peroxide at high concentrations and high pH values and an important reason for incomplete bleaching is low pH values that do not fully activate the hydrogen

20   peroxide to the hydrogen peroxide anion. Furthermore, peroxide degradation leads to pulp yellowing and darkening processes. The optimum bleaching process then is one at which the bleaching occurs at the highest levels of peroxide anion concentration that are consistent with the beneficial effects of bleaching but which exclude the negative effects of peroxide degradation.

25   3. A strategy of maximizing the relative concentration of the peroxide (HOO^-) bleaching agent and the beneficial effects of the bleaching agent of color removal are taught in accordance with an embodiment of the present invention. This method does not require a multiple regression with respect to a concentration in the effluent. A learning step with respect to the final pulp properties is advantageous but not necessary.

30

As of yet, reliable means for determining hydrogen peroxide concentration are not available. The value of hydrogen peroxide consumed at a paper mill is typically between two and ten million dollars a year. Much of this peroxide is wasted and the development of a reliable means for monitoring hydrogen peroxide in the pulp and paper industry is

5 important in making the bleaching process more economical. The advantages of using a set of UV absorbance or alternatively Raman scattering ratios obtained from a filtrate to determine the peroxide concentration have not been previously recognized. A simple measurement of the hydrogen peroxide ion concentration as a function of UV absorbance or Raman emission would be obvious. However, the measurement of the hydrogen

10 peroxide concentration in a background of strongly UV absorbing substances, such as lignin, presents substantial deconvolution problems. Furthermore, the measurement of the peroxide concentration under pH conditions where the relative amounts of hydrogen peroxide and the hydrogen peroxide concentrations are varying is a difficult problem. The present invention obviates this problem, in that by using ratios, i.e. relative values,

15 obtained from ultraviolet-visible measurements the contributions from lignin and the variation due to pH are factored out.

A plurality of different methods for measuring peroxides are known. Among those, polarigraphic measurements are thought to be unreliable and commercial methods using

20 catalytic peroxide decomposition were not yet available. Presently, a hydrogen peroxide measurement is available from BTG a Division of Spectris Technologies, but the reliability of this measurement is still in question and it has not been widely adapted.

In accordance with the present invention ratios of Raman peak intensities are used to

25 predict the properties of a solution or a solid such as pulp that is processed with the solution. The method and apparatus of the present invention extend the multiple ratio strategy to Raman scattering intensities observed at visible or near IR wavelengths. In this case the intensity of the Raman shifted data is used to create the ratio. These intensities are related to the concentration of species dissolved in the liquid. A preferred

30 measurement is using a transmissive Raman scattering measurement using a Nd:YAG

27

(1064 nm) laser to minimize sample fluorescence. If desired, baseline corrected spectra and a scattering from a water reference is subtracted before extraction of intensities for ratios. The Raman scattering intensities provide a good measure of the concentration of small oxygenated molecules. Relevant small molecules and complex ions in the pulp and

5   paper industry include, but are not exhaustive, SO_4^{2-}, SO_3^{2-}, H_2O_2, ClO2, HClO3, silicates, acetic acid, Chloric Acid HClO3, Chlorate ClO3(-), Chlorous Acid HClO2, Chlorite ClO2(-), Hypochlorous Acid HClO. Hypochlorite ClO(-), phosphate, nitrate, nitrites. If desired, the present invention is used to measure large molecules such as hemicellulose, extractives and pectic substances. The use of Raman spectra to measure small,

10   oxygenated molecules is well documented and extensive lists exist of Raman shifts for molecules and functional groups, which are found for example in *"Infrared and Raman Spectra of Inorganic and Coordination Compounds Part A: Theory and Applications in Inorganic Chemistry"* Kazuo Nakamoto, 1997, John Wiley and Sons, Inc, New York. The value of using Raman emissions to measure and control species of oxidative and

15   reductive oxygenated inorganic species has not been recognized before this invention. Furthermore, the importance of measurement of the relative concentrations of different related species, for example: HOOH and HOO- or ClO_2, ClO_2^-, HClO and ClO_3^- or $S_2O_4^{2-}$, SO_3^{2-}, SO_4^{2-}, has not been recognized or adapted.

20   Figure 7 shows an example of dispersive and Fourier Transform (FT) Raman spectra to demonstrate an interference using a laser at shorter wavelengths. The plot presents Raman data from a dispersive system with a 514.5 nm laser and a FT system with a 1064 nm laser. The data from the dispersive system shows interference that probably is due to fluorescence, at 800-1000 cm^{-1}. With advances in Raman spectroscopy lasers at a longer

25   wavelength than 514.5 nm are used to obviate a fluorescence problem. Thus a preferred configuration in accordance with an embodiment of the present invention is a laser operating at a higher wavelength than 514.5 nm.

Figure 8 shows a Fourier Transform (FT) scan of a Raman scattering signal from a pulp

30   bleaching mixture of hydrogen peroxide, silicate, and sulfate. Steps in the processing of

the raw data include a fast Fourier transform, a baseline correction and then subtraction of the water signal. The peak at 400 cm⁻¹ and below is an experimental artifact due to a silicate cell and the detection geometry. An optimized system would have a different geometry, such as 90 degree detection, or cell material, such as sapphire, to minimize the

5   interference of the cell material when measuring silicate solutions and colloids.

Figure 9 shows a series of Raman spectra of pressates from peroxide bleaching of pulp. These spectra were obtained using a 1064 nm laser with FT signal processing, baseline correction and subtraction of water spectra. The samples were quantitatively diluted to

10   pH 7 before their measurement. The series progresses from high bleaching pH at the top to low bleaching pH at the bottom. Raman peaks are observed at approximately 530 cm⁻¹ for silicate, at approximately 877 cm⁻¹ for hydrogen peroxide (H_2O_2 , at approximately 990 cm⁻1 for sulfate, and at approximately 1077 cm⁻¹ for and carbonate. The Raman peaks for sulfate shown in Figure 8 appear due to the addition of sulfate. Sulfate was

15   added in order to lower the pH value. The Raman peaks for carbonate are observed because CO_2 is absorbed from the surrounding atmosphere to form carbonate ions. Alternatively, this method is used for predicting scale formation since it is capable of detecting sulfate ions and carbonate ions. In this case, care is taken that the pressates are not exposed to carbon dioxide.

20

Table 2 shows a relationship between pulp yield and Raman intensity ratios.

Table 2

Regression Summary for Dependent Variable: YIELD

25   R= .99912365 R^2= .99824807 Adjusted R^2= .99562018
$F_{(3,2)}$=379.87 p<.00263 Std.Error of estimate: .27325

	BETA	St. Err. of BETA	B	St. Err. of B	t(2)	p-level
Intercpt			37.37	4.841	7.72089	.016364
RH2O2U V2	.992604	.080541	8322.67	675.313	12.32417	.006520
H2O2	.958102	.091885	32733.36	3139.227	10.42720	.009072
RSILH2O	.942172	.122940	38.20	4.985	7.66366	.016604

2						

Table 3 shows a relationship between residual hydrogen peroxide and Raman ratios.

Table 3

5   Regression Summary for Dependent Variable: H2O2 residual
R= .99822460 R^2= .99645235 Adjusted R^2= .99113086
$F_{(3,2)}$=187.25 p<.00532 Std.Error of estimate: .11298

	BETA	St. Err. of BETA	B	St. Err. of B	t(2)	p-level
Intercpt			-12.085	1.7914	-6.74606	.021275
RH2O2UV2	1.045293	.122605	2546.622	298.7004	8.52567	.013480
RH2O2SIL	1.376609	.171798	1.718	.2144	8.01298	.015220
RSILH2O2	1.395214	.236563	16.437	2.7869	5.89786	.027565

10   Figure 10 shows a matrix plot for Aspen TMP pulp bleaching with hydrogen peroxide
and the pulp and bleaching pressate properties. This matrix plot shows variables
describing the peroxide bleaching process and Raman peak intensity and intensity ratios
from bleaching pressates obtained by bleaching with hydrogen peroxide under varied pH
conditions. The samples were diluted to a constant pH before measurement so that the
15   information in them relates to changes developed during the bleaching process. The pulp
variables include an ultimate brightness, bulk, which is a measure of the specific volume
of the pulp, and yield, which is the % mass of the bleached pulp relative to the
unbleached pulp. The bleaching pressate values are characterized by the process variable
pH, the residual peroxide as a % on pulp when 4% by weight of peroxide and pulp that
20   was initially put on the pulp, and the total dissolved solids (TDS). Raman intensity ratios
provided relate to the peak intensity for silicates at ~530 cm^{-1} (silicate, ~530 cm^{-1}), and
hydrogen peroxide at 877 cm^{-1} (H_2O_2, 877 cm^{-1}). The Raman intensity ratio of
RH2O2SIL presented in Figure 10 is a ratio of (H_2O_2 (877 cm^{-1}) intensity/ intensity of
silicate (~530 cm^{-1}) and intensity of Raman intensity to UV absorbance is given by the

following ratio RH2O2UV2 as expressed by (H_2O_2 (877cm^{-1})/UV absorbance at 280 nm). For each subplot the X-axis relates to the relative concentration of the variable above and the Y-axis relates to the relative concentration of the variable to the right.

5   The ratio formulated between the Raman peak intensity for the peroxide and the silicate is of importance for indicating an optimal stabilizing effect through the silicate. Silicate is added to the bleaching solution to stabilize the peroxide. Thus the amount of silicate with resoect to hydrogen peroxide is maximized such that it provides best stabilizing effects for the amount of hydrogen peroxide.

10

Table 4 shows data for peroxide bleaching at different pH values. The Raman intensity ratios are compared to pulp and pressate properties.

Table 4

15

	Pulp and Pressate Properties					Raman intensities of pH adjusted pressate			
Start pH	Bleach Yield	H2O2 residual	TDS g/l	rightne ISO	Pulp Bulk	Silicate 530 cm-1	H2O2 877 cm-1	SO4 990 cm-1	CO3 1077 cm-1
9.5	97.2	3.47	1.17	73.84	3.27	0.25	1.18	1.28	0.96
9.7	96.1		1.16	74.52	3.17	0.28	1.05	1.27	0.92
10.0	96.0	2.38	1.76	77.97	3.12	0.32	1.08	1.29	1.04
10.3	93.6	2.82	1.95	78.93	2.80	0.21	1.06	1.24	0.97
10.5	92.8	1.90	2.21	78.99	2.92	0.20	1.05	1.24	0.96
10.7	93.0	1.89	2.20	79.68	2.38	0.32	0.98	1.34	0.91
11.1	90.2	1.26	2.69	81.82	2.60	0.30	0.98	1.28	0.94
11.5	88.9	0.91	3.15	83.45	2.00	0.40	0.86	1.46	1.01
12.1	86.7	0.04	5.26	80.33	1.69	0.41	0.89	1.38	0.97

Figure 11 presents Raman Spectra of pressates from hydrogen peroxide bleaching of aspen TMP pulp at different pH values. The spectra are obtained directly, i.e. without

20   dilution or pH adjustment. The Raman peaks for hydrogen peroxide (H2O2) at 877 cm^{-1}, for carboxylic acid (COO-) at 924. cm^{-1} , for a C-H bending mode at 1350 cm^{-1}, and for a C-H vending mode at 1415 cm^{-1} are shown. The relative decrease of the hydrogen peroxide peak and increase in the peaks representing different bleaching by-products can be related to pulp properties developed during bleaching. During the pulp bleaching

process with hydrogen peroxide competing chemical processes result in the destruction of colored species, the cleavage and removal of colored species, and the formation of colored species during non-productive cleavage of lignin substances. Peroxide concentrations decrease during both productive and non-productive reactions through

5   bimolecular degradation of the peroxide or reaction with the wood substances. The spectra in figure 11 and the associated tables 5 and 6 below, show that the productive reactions leading to high brightness with minimal loss of yield and bulk generate carboxylic groups with Raman intensities at 924 cm^{-1}. Smaller amounts of brightness gain and greater yield or bulk loss correlate well with the increase in the intensity of

10   Raman emission peaks at 1350 cm^{-1} and 1415 cm^{-1}. Hence the greatest improvement in brightness gain with the least lost of yield or bulk occurs when the amplitude of the intensity ratio of the peak at 924 cm^{-1} to the intensity at 1350 cm^{-1} or 1415 cm^{-1} is maximized. The peak intensity for the hydrogen peroxide at 877 cm^{-1} should be maximized to preserve the hydrogen peroxide and to prevent unnecessary radical

15   reactions. These results provide a basis for improved relationships between the Raman intensities and the pulp properties shown in Tables 7-12. In Table 7 the brightness development is optimized when the relative consumption of the hydrogen peroxide to the development of the C-H peak at 1350 cm -1 is minimized. In Table 9 the relates the bulk to the product of the peaks at 1350 cm -1 and 1415 cm -1 as formation of compounds

20   contributing to these both of these peaks contribute to brightness loss.

Table 5

PH initial	final	ISO % brightness	freeness	bulk	H2o2 % in pressate	% on pulp	TOC	yield
9.3	6.4	72.17	164.5	2.931	0.577	2.974	1580	98.102
9.6	6.5	72.56	149	2.967	0.548	2.825	1550	98.138
10	7.1	74.49	148	2.901	0.359	1.850	3030	96.361
10.2	7.3	75.17	143	2.774	0.311	1.604	3610	95.664
10.5	7.4	76.05	147	2.750	0.277	1.428	4070	95.112
10.7	7.6	76.03	152	2.815	0.245	1.262	4570	94.511
11	8	77.58	142	2.620	0.147	0.760	6550	92.133
11.4	8.4	78.32	132	2.453	0.088	0.451	6400	92.313
11.8	9	78.25	129	1.954	0.075	0.388	13100	84.266

Table 6

PH		UV ABS	Raman Intensities			
initial	final	280 nm	I_876	I_I924	I_1350	I_1415
9.3	6.4	0.588	1.960	0.532	0.364	0.496
9.6	6.5	0.578	1.585	0.434	0.263	0.409
10	7.1	0.867	1.207	0.779	0.334	0.666
10.2	7.3	1.013	0.996	0.893	0.441	0.653
10.5	7.4	1.183	0.888	0.964	0.469	0.797
10.7	7.6	1.269	0.797	0.971	0.471	0.795
11	8	2.164	0.656	1.559	0.731	1.181
11.4	8.4	3.193	0.324	1.647	0.877	1.334
11.8	9	4.371	0.587	1.782	1.216	1.750

Figure 12 shows a graph for the prediction of pulp brightness from a model based on a combination of Raman peak intensities and Raman peak intensity ratios. The observed values are plotted against the predicted values with the ISO brightness being a dependent variable and the independent variables being the Raman intensities and intensity ratios.

Tables 7 to 12 below demonstrate the prediction of pulp properties from Raman ratios and Raman intensities. The pulp properties presented are brightness in Table 7, bulk in Tables 8 and 9, residual hydrogen peroxide on the pulp in Table 10, and total organic carbon (TOC) in Tables 11 and 12.

Table 7

Regression Summary for Dependent Variable:**Brightness**
R= .99774854 R²= .99550215 Adjusted R²= .99280344
F(3,5)=368.88 p<.00000 Std.Error of estimate: .19239

Raman		St. Err.		St. Err.		
Intensity	BETA	of BETA	B	of B	t(5)	p-level
Intercept			77.16	.4319	178.6687	.000000
I876/I1350	-.318581	.111927	-.35	.1226	-2.8463	.035979
I1415	.279821	.054338	750.02	145.6442	5.1497	.003616
I876	-.444773	.102212	-1016.37	233.5693	-4.3515	.007349

Table 8

Regression Summary for Dependent Variable: **BULK**
R= .98249292 R²= .96529234 Adjusted R²= .96033411

33

F(1,7)=194.68 p<.00000 Std.Error of estimate: .06333

	BETA	St. Err. of BETA	B	St. Err. of B	t(7)	p-level
Intercpt			3.264	.04657	70.0903	.000000
I1350	-.982493	.070415	-521.783	37.39594	-13.9529	.000002

Table 9

The Ratio Predicts bulk better

Regression Summary for Dependent Variable: **BULK**
R= .99113735 R²= .98235324 Adjusted R²= .97983227
F(1,7)=389.67 p<.00000 Std.Error of estimate: .04516

	BETA	St. Err. of BETA	B	St. Err. of B	t(7)	p-level
Intercpt			3.	.022	138.9712	.000000
P1350141	-.991137	.050209	-127757.	6471.954	-19.7401	.000000

Table 10

Regression Summary for Dependent Variable: **H2O2 residual on Pulp**
R= .99806738 R²= .99613850 Adjusted R²= .99382159
F(3,5)=429.94 p<.00000 Std.Error of estimate: .07356

	BETA	St. Err. of BETA	B	St. Err. of B	t(5)	p-level
Intercpt			.799	.16514	4.84114	.004710
R8761350	.360850	.103708	.163	.04689	3.47948	.017669
I1415	-.252501	.050347	-279.289	55.68855	-5.01519	.004052
I876	.427770	.094706	403.384	89.30762	4.51680	.006301

Table 11

Regression Summary for Dependent Variable: **TOC**
R= .96431621 R²= .92990576 Adjusted R²= .91989230
F(1,7)=92.866 p<.00003 Std.Error of estimate: 1002.7

	BETA	St. Err. of BETA	B	St. Err. of B	t(7)	p-level
Intercpt			-1394.	737.4	-1.89022	.100643
I1350	.964316	.100067	5705570.	592068.1	9.63668	.000027

Table 12

Regression Summary for Dependent Variable: **TOC**
R= .99132396 R²= .98272319 Adjusted R²= .97235711

F(3,5)=94.802 p<.00008 Std.Error of estimate: 589.00

		St. Err.		St. Err.		
	BETA	of BETA	B	of B	t(5)	p-level
Intercept			-1989.	1509.	-1.31791	.244683
Product I1350•I1415	2.031475	.447598	29173073 E2	64277456 6.	4.53862	.006177
Ratio I1924/I1350	.208308	.072085	2406.	832.	2.88976	.034197
UV280 abs	-.993688	.435777	-2691.	1180.	-2.28027	.071514

Figure 13 presents the Raman spectra showing HOO⁻ and HOOH peaks at 850 cm⁻¹ and

877 cm⁻¹, respectively. The spectra presented in Figure 13 are shown after subtraction of

a reference spectrum of water and baseline correction. When looking at the Raman

spectrum of hydrogen peroxide two peaks are observed for peroxides. The intensity of

the two peaks varies with the pH value of the solution, i.e. at a lower pH value more

hydrogen peroxide is observed and at a higher pH value more peroxyl anion (HOO⁻) is

observed as a result of ionization of the hydrogen peroxide. In bleaching processes it is

important to know what percentage of the hydrogen peroxide is ionized at a particular pH

value. This is determined by looking at the two Raman peaks at 850 cm⁻¹ and 877 cm⁻¹

and comparing them with each other. The active species in bleaching processes are the

ionized species and thus the amount of peroxyl anion (HOO⁻) needs to be maximized

since too much peroxyl anion (HOO⁻) would cause a degradation of the hydrogen

peroxide. In accordance with an embodiment of the present invention Raman

spectroscopy conveniently provides a means for determining an extent of ionization of

hydrogen peroxide by comparing the Raman peaks for the peroxyl anion and hydrogen

peroxide.

Figure 14 shows a matrix plot of Raman intensities and Raman ratios as a function of pH.

The considered Raman intensities are the Raman intensities for hydrogen peroxide

HOOH (I877) and peroxyl ions HOO⁻ (I850) as a function of pH. Two ratios of Raman

peak intensities are also shown in the matrix plot. The Raman intensity ratio of R850877 is the intensity of the peak at 850 cm^{-1} to the intensity of the peak at 877 cm^{-1}, the Raman intensity ratio R877T is the ration of the 877 cm^{-1} peak to the sum of the two peak intensities at 850 cm^{-1} and 877 cm^{-1}. These intensity ratios give new non-linear variables

5   that relate to the peroxide solutions properties. The matrix plot shows the relationship between the brightness and the Raman peak intensities of the HOO- and HOOH peroxide species. The use of these peak intensities for the measurement and control of hydrogen peroxide concentrations in pulp and paper and water treatment has not been described. Thus in accordance with an embodiment of the present invention the Raman peak

10   intensities of the Raman peaks at 850 cm^{-1} and 877 cm^{-1} are used to control the hydrogen peroxide concentration. The ratio of the peak intensities provides a new relationship with respect to the solution properties as shown in plot 14C. The ratio is different than the direct peak intensities as shown in Figures 14F and 14H. Raman peak intensity ratios or products provide different means the properties are modeled by influencing variables. A

15   second ratio may be defined by the intensity of one peak to the sum of the intensity of both Raman peaks. This ratio is expected to follow relationships relavant to the pKa of the peroxide.

The matrix plot presented in Figure 14 does not show a product of the intensities of the

20   two Raman peak intensities at 850 cm^{-1} and 877 cm^{-1} . However, the product of these two Raman peak intensities provides similar results as the ratio between two Raman peak intensities.

The Measurement of the Redox Properties and Relative Concentrations of Related Oxidative and Reductive Species

25   Figures 15 and 16 show Raman spectra of different sulfur oxianion in a dibasic form.

Figure 17 presents spectra showing Raman intensities of a solution of sodium hydrosulfite ($Na_2S_2O_4$) oxidizing to sulfate and sulfite ions. The management of oxidizing and reducing substances in industrial applications is problematic in part

30   because measures such as an oxidation reduction potential (ORP) are very sensitive to

pH, ionic strength, temperature and the influence of interfering substances. The use of Raman peak intensities provides a means to directly measure the concentrations and relative concentrations of the different species contributing to the oxidation potential of the solution.

5

Figure 18 shows the S-O stretching region of the Raman spectrum during the oxidation of hydrosulfite to sulfate. The isobestic point is the point at which the total concentration is always a same function of intensity no matter what proportion of the two different species, i.e. hydrosulfite and sulfate, are present.

10

Figure 19 presents a matrix plot showing Raman intensities, and Raman intensity ratios with time and oxidation reduction potential (ORP). Regression lines marked in the matrix plot of Figure 19 demonstrate that the Raman intensity ratios correlate better with the ORP than their components. Plots *P* and *R* within Figure 19 demonstrate that a

15 Raman intensity ratio provides the best direct measure of the ORP of the sulfur species in solution since these plots are almost linear.

Table 13 provides a regression summary for the oxidation reduction potential and Table 14 shows the correlations for hydrosulfite oxidation.

20

Table 13

Regression Summary for Dependent Variable: ORP
R= .99514836 R²= .99032025 Adjusted R²= .98709366
F(1,3)=306.93 p<.00041 Std.Error of estimate: 6.0576

	BETA	St. Err. of BETA	B	St. Err. of B	t(3)	p-level
Intercept			-206.467	9.147723	-22.5703	.000190
Ratio I460/I977	-.995148	.056803	-75.062	4.284508	-17.5193	.000405

25 ORP=-206.467-75.062*I460/I977

Table 14

Correlations Hydrosulfite Oxidation

Marked correlations are significant at p < .05000

	time	ORP	I228	I460	I583	I977	I998	I1022	Ratio 583 977	Ratio 977 998	Ratio 460 977	Ratio 977 1022
TIME	1.00	.94	-1.00	-.99	-1.00	.94	-1.00	-.79	-.94	.90	-.94	.90
ORP	.94	1.00	-.98	-.99	-.95	.97	-.88	-.96	-.99	.93	-1.00	.96
I228	-1.00	-.98	1.00	1.00	1.00	-.94	.99	.79	.94	-.91	.94	-.90
I460	-.99	-.99	1.00	1.00	1.00	-.94	.99	.79	.96	-.89	.96	-.89
I583	-1.00	-.95	1.00	1.00	1.00	-.94	1.00	.79	.96	-.89	.95	-.89
I977	.94	.97	-.94	-.94	-.94	1.00	-.95	-.93	-.87	.98	-.87	.99
I998	-1.00	-.88	.99	.99	1.00	-.95	1.00	.81	.95	-.91	.94	-.91
I1022	-.79	-.96	.79	.79	.79	-.93	.81	1.00	.75	-.91	.76	-.96
Ratio 583 977	-.94	-.99	.94	.96	.96	-.87	.95	.75	1.00	-.77	1.00	-.81
Ratio 977 998	.90	.93	-.91	-.89	-.89	.98	-.91	-.91	-.77	1.00	-.77	.99
Ratio 460 977	-.94	-1.00	.94	.96	.95	-.87	.94	.76	1.00	-.77	1.00	-.80
Ratio 977 1022	.90	.96	-.90	-.89	-.89	.99	-.91	-.96	-.81	.99	-.80	1.00

The Oxidation/Reduction Potential (ORP) is a measurement of the potential for a reaction to occur. Oxidation-Reduction represents electron concentration and activity level. An ORP in the plus range indicates oxidation, i.e. the absence of energy, and an inability to perform additional chemical reactions. An ORP in the negative range indicates chemical reduction, i.e. the presence of electrons, potential energy, and the ability to generate additional chemical reactions. ORP is therefore a measure of energy potential. The more

negative the ORP, the more electrons present (in relation to the number of protons), and the more energy available. Biological redox reactions are a result of hydrogen being the essential electron donor, and oxygen being the essential electron acceptor.

5   Oxidation reduction potential, ORP, measurements are used to determine the oxidizing or reducing properties of a solution. Typical applications include the neutralization of waste water containing sulfides, cyanides, chromates, nitrites or organic waste and controlling the addition of oxidants to drinking water, swimming pools or cooling towers. ORP can also be used to determine the ion activity of metals in solution and determine the endpoint

10   of titrations.

The standard method for determining the ORP is given in "Standard Methods for the Examination of Water and Waste Water", 18th Edition, 1992, method 2580 B. Discussion of relevant background information is included in this reference.

15

The term potential of an oxidative reductive process within this specification is defined as the oxidation reduction potential and also as an oxidation reduction indicator. The potential of an oxidative reductive process is a measure of a composite state of the oxidation reduction capacity of a sample and not of the oxidative reductive capacity of

20   the individual species.

ORP is commonly measured as pE using a metal electrode, a reference electrode and a high input impedance millivolt meter such as a pH meter. However, electrochemical methods for measuring the ORP cannot discriminate between different

25   oxidative/reductive species. In the environment or in industrial applications usually many different influences on the ORP from other oxidative or reductive species are present. In accordance with an embodiment of the present invention Raman spectroscopy is employed to determine the contribution to ORP of certain species more accurately by monitoring the oxidative/reductive properties and relative concentrations of the species of

30   interest. Alternatively, additional oxidative/reductive species contributing to the ORP are

monitored if their molecular vibrations are Raman active.

The Nernst equation relates the oxidative and reductive properties of a certain regime. The Nernst equation can be expressed in pE notations as:

5

$$pE = pE^- + \frac{1}{n}\log_{10}\frac{\{A_{OX}\}}{\{Ared\}}$$ [1]

pE is a notation related to the oxidation form and the reduction form of the species in a regime. Presented below is the example for a water regime.

The limit of pE in water can be determined using the Nernst equation. The stability

10   regime of water is determined by the reduction and oxidation of water. The reduction of water defines the lower limit to pE

$$H^+ + e^- \rightarrow \frac{1}{2}H_2O$$ [2]

15

$$pE = pE^- + \log_{10}\frac{\{H^+\}}{f_{H2}^{\frac{1}{2}}}$$ [3]

As pE⁻ is zero by definition and the boundary condition commonly used is a hydrogen fugacity, f_{H2} of unity, this gives

20

$$pE = -pH$$ [4]

The upper boundary for the stability of water is given by the oxidation reaction:

$$\frac{1}{4}O_2 + H^+ + e^- \rightarrow \frac{1}{2}H_2O$$ [5]

25

$$pE = pE^- + \log_{10} f_{O2}^{\frac{1}{2}}\{H^+\}$$ [6]

The boundary condition used is an oxygen fugacity of unity. The upper pE limit becomes:

$$pE = 20.75 - pH \qquad [7]$$

The pE for natural waters can be calculated using equation [6]. The unknowns which must be measured are pH and the O2 partial pressure (concentration). For example, the pE for surface water in equilibrium with the atmosphere (p_{O2} = 0.21 atm) and have a pH of 8 would be:

$$pE = pE^- + \log_{10} f_{O2}^{1/4} \{H^+\} \qquad [8]$$

$$pE = pE^- - pH + \log_{10} f_{O2}^{1/2} \qquad [9]$$

$$pE = 20.75 - 8 + \log_{10}(0.21)^{1/4} = 12.58 \qquad [10]$$

The stability boundaries for water were calculated earlier. The upper and lower limits, respectively, are:

$$pE = 20.75 - pH \qquad [11]$$
$$pE = -pH \qquad [12]$$

Measurements of Properties of Species Forming Complexes, Polymerized and Networked Structures, and Multiple degrees of Ionization.

Figure 20 presents a series of silicate Raman spectra as a function of varying hydroxide concentration as taken from Prabir K. Dutta and Dah-Chung Shieh, published in Applied Spectroscopy, Vol. 39, No. 2, pp. 343-346 (1985). These spectra yield the intensities and ratios presented in Figures 21 and 22. Silicates can take different structural forms

through ionization and polymerization in dependence upon a pH value. Silicates can be used in a plurality of industrial applications. For example, silicates are added to a bleaching solution in order to stabilize peroxides.

5   The set of spectra shows how silicate types vary with solution conditions.

Figure 21 shows the intensities of the different peaks as derived from the spectra presented in Figure 20. Figure 21 shows a matrix plot of Raman intensities as a function of the HO$^-$/Si ratio as derived from Prabir K. Dutta and Dah-Chung Shieh, Applied

10   Spectroscopy, Vol. 39, No. 2, 343-346 (1985). Peaks from silicate relate to different vibrational modes that depend on the ionization and degree of polymerization of the silicate. Vibrations from silicate monomers yield peaks at 925 cm^{-1} (Si-O$^-$ stretch, monomer ionized) 772 cm^{-1} (Si-O-H stretch, monomer not ionized), 482 cm^{-1} (Si-OH stretch) and 446 cm^{-1} (SiO$_2$(OH)$_2^{2-}$ symmetric bend). Dimer groups yield peaks at 598

15   cm^{-1} (Si-O-Si stretch, dimer bridge) and 1014 cm^{-1} (SiO3 stretch, dimer endgroup). Cyclic trimers have a breathing vibration at 531 cm^{-1}. The peak at 1014 cm^{-1} (SiO3 stretch, dimer endgroup) shifts to ~1030 cm^{-1} with cyclic trimers.

The prior art has looked only at the Raman intensities. In accordance with the present

20   invention ratios are used as they are capable of presenting different non-linear relationships with respect to solution properties than the intensities do.

Ratios present the physical properties of the silicates better than intensities alone do. This is demonstrated in Figure 22 showing a matrix plot of Raman intensity ratios as a

25   function of the HO$^-$/Si ratio from Prabir K. Dutta and Dah-Chung Shieh, *Applied Spectroscopy*, Vol. 39, No. 2, 343-346 (1985). It is noted that this article does not teach the use of ratios. The intensities given in this article were used to derive Raman intensity ratios in order to demonstrate that the use of Raman intensity ratios is much better in predicting the physical properties of silicates. The ratios relate the relative concentrations

30   of different functional groups characterizing the silicate speciation. These ratios provide

new variables that logically relate to the properties of the silicate solution. The ratio R579/1014 is related to the degree of polmerization or the chain length because individual intensities represent the amount of bridging/the amount of end groups, i.e. ratio of the peak intensity at 597 cm^{-1} to the intensity at 1014 cm^{-1}. The degree of

5   polymerization decreases with increasing alkali concentration. The ratio R925/772 is related to the degree of amount of ionization of the silicate monomers (ratio of the peak intensity at 925 cm^{-1} to the intensity at 772 cm^{-1}). The ratio R531/597 is related to the ratio of cyclic trimer groups to dimer groups (ratio of the peak intensity at 531 cm^{-1} to the intensity at 597 cm^{-1}). The ratio R531/772 is related to the ratio of cyclic trimer groups to

10   protonated monomer groups (ratio of the peak intensity at 531 cm^{-1} to the intensity at 772 cm^{-1}). The ratio R531/925 is related to the ratio of cyclic trimer groups to ionized monomer groups (ratio of the peak intensity at 531 cm^{-1} to the intensity at 925 cm^{-1}). The ratio R1014/925 is related to the ratio of ionized dimer groups to ionized monomer groups (ratio of the peak intensity at 1014 cm^{-1} to the intensity at 925 cm^{-1}).

15

FT-Raman spectra were recorded using a Bruker IFS-88 Fourier Transform Infrared (FT-IR) spectrometer equipped with FRA 106 Raman accessory. Excitation was provided by an Nd:YAG laser (λ = 1.064mm, v =9394 cm^{-1}). Solid state samples were measured using an aluminum sample holder and solutions were contained in a 0.5 cm cuvettes.

20   Sepctra were recorded at a resolution of 4 cm^{-1}, utilizing a laser power typical 50mw for a solid sample and 280mw for a solution sample.

The spectrum in solid-state is different from the spectrum from the solution. In most cases an aqueous solution was measured. In general, Raman spectroscopy has an

25   advantage over IR spectroscopy with respect to working on an aqueous phase. The detection limit can be pushed down to ~0.05% at current experimental conditions (Laser power 280mw and single path at 180° sample collection configurations). In order to increase the detection limit, higher laser power and/or multi-path sample collection configuration are needed in FT-Raman spectroscopy.

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Example of The Use of Raman Spectra and Ratios for Measurement and Control of Pulp Bleaching.

There are 10 different samples (PH = 9.5, 9.7, 10.0, 10.3, 10.5, 10.7 11.5, 11.7, 12.1 and 12.7). Since each sample adjust the final pH by using buffer solution (pH = 6.9) and 1M NaOH, these 10 sample have been divided into two groups. There is one group with three peaks at 877, 990 and 1077 cm^{-1}, and another group having two broad bands at 1100 and 1630 cm^{-1}. These two broad bands are due to water and the Raman sample cell. As described above, water was subtracted from the obtained Raman spectra before processing the data.

According to the reference Raman spectra of H_2O_2, the peak at 877 cm^{-1} in bleaching water is due to the H_2O_2. The amount of the H_2O_2 is approximately 0.1%. The peak at 990 cm^{-1} is due to SO_4 stretching band of the sulfate (reference see previous work). The amount of H_2O_2 decreases with the pH increase, while the amount of the sulfate increases with the pH increase. The detection limit for H_2O_2 and SO_4 can be lowered down to 0.1% at current instrument condition. Interfering peaks due to carboxylic acid vibrations occur at 890 cm^{-1} for acetic acid and 927 cm^{-1} for the acetate ion.

The third peak in bleaching water sample is at 1077 cm^{-1}. The intensity of this peak does not change with pH increase.

Other Examples of Raman Spectra of Ultrafiltered Pulp Processing Waters

Raman spectra of two white water samples from Millar Western Pulp (MWP) and one from Alberta Newsprint (ANC) are collected and shown in Figure 23. These samples are filtered through a 0.45 micron filter before data is collected. Only one band at 990 cm^{-1} appears in ANC water. It is the contribution of the SO_4 (sulfate ion) band from the sulfate. There are also some sulfates in two kinds of Millar Western Pulp water. The amount of sulfate is different according to the band intensities. The peak at 877 cm^{-1} in both Millar Western Pulp water samples also indicates the existence of H_2O_2. Another band at 925 cm^{-1} in two MWP water samples is possibly the contribution of the acetate

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buffer solution. Figure 24 gives the Raman and IR spectra of acetic acid and acetic buffer solution (0.05M). The amounts of the buffer solution are different in these two kinds of different water samples.

5   Other relevant small molecules and complex ions in the pulp and paper industry may be detected. These species include SO_4^{2-}, SO_3^{2-}, H_2O_2, ClO2, HClO3, silicates, acetic acid, Chloric Acid HClO3, Chlorate ClO3(-), Chlorous Acid HClO2, Chlorite ClO2(-), Hypochlorous Acid HClO. Hypochlorite ClO(-), phosphate, nitrate, nitrites

10   **Assignments from organic model compounds**

1800-1600 cm^{-1} region: The stretching bands of C=O from –COOH groups were shown up in spectra of Glucuronic acid and Polygalacturonic acid.

1500-1000 cm^{-1} region: The CH bending bands of the relevant R groups are in this region

15   except for one band at ~1330 cm^{-1} is due to the –OH bending. The CO stretching bands from different groups appear in 1200-1000 cm-1 region.

1000-300 cm^{-1} region: The bands appear from 1000-700 cm^{-1} are due to different CH bonds wagging or scissoring modes. Most bands below 700 cm^{-1} are due to molecular

20   skeletal deformations.

Raman spectrum of Vanillin in solid-state show two more CH stretching bands at 3077 and 3030 cm^{-1} belong to aromatic C-H bonds. Three bands at 1662, 1589 and 1508 cm^{-1} are due to the different C=C bond stretching modes. These are main different

25   characteristic bands between lignin and carbohydrates. PAS-IR spectrum of Kraft lignin is shown in Figure 2b. The strong –OH absorbent band and other hydrogen bonding absorbent bands in IR spectrum have strong negative effect on spectral quality. In order to avoid the disturbance from the –OH groups and hydrogen bonds in IR spectra, Raman data would be a good choice to work on.

30

Raman spectra of tristerain and abietic acid were obtained. These two compounds belong to the wood extractive categories. Raman spectra of these two compounds are typical fatty acids with different chain length. By simply comparing the intensities of $v_{C=O}$ bands at ~1700 cm^{-1} with the intensities of the CH stretching bands at 2800-3100 cm^{-1}, the chain

5   length of abietic acid is shorter than tristerarin.

The invention provides an additional set of process parameters that are closely tied to the process chemistry. Using these new variables with functions that predict, model and control the state and outcome of a multi-dimensional process provides a significant advantage over

10   standard chemometric and linear regression methods. Advanced control systems including those utilizing fuzzy logic, time correlation analysis, neural networks, adaptive control, principle component analysis and partial least squares provides a means of developing software programming and logic solutions to problems with a high dimensionality. It is an object of this invention to provide new variables that may be used to better control input and

15   output parameters in a complicated process with many interrelated variables.

The above-described embodiments of the invention are intended to be examples of the present invention and alterations and modifications may be affected thereto, by those of skill in the art, without departing from the scope of the invention which is defined solely

20   by the claims appended hereto.

Claims

1. A method for measuring an amount of peroxide or peroxyl ion of a sample comprising the following steps:

   (a) irradiating at least a portion of the sample with a laser light for generating a Raman spectrum of the sample;

   (b) obtaining at least two measurements at two different wavenumbers from the Raman spectrum, a first measurement related to a Raman intensity related to an amount of peroxide or an amount of peroxyl ion, the second measurement related to the other of the amount of hydrogen peroxide and the amount of peroxyl ion; and

   (c) formulating a relationship between a Raman intensity for hydrogen peroxide and a Raman intensity for the peroxyl ion by comparing information related to the two measurements for determining the amount of peroxide or peroxyl ion.

2. A method as defined in claim 1 wherein the relationship between the Raman intensity for peroxide and the peroxyl ion is at least one of a product, a ratio, and a sum of the two measurements.

3. A method as defined in claim 2 further comprising the step of varying the amount of peroxyl ion by varying a pH of a solution.

4. A method as defined in claim 3 wherein an extent of bleaching is determined from the relationship, said extent of bleaching being related to an amount of peroxide or peroxyl ion.

5. A method as defined in claim 3 wherein an extent of ionisation of peroxide is determined from a non-linear relationship including a ratio between the Raman intensity of peroxide and the peroxyl ion.

6. A method as defined in claim 2 wherein the Raman intensity for peroxide is obtained at approximately 875 cm^{-1} and the Raman intensity for the peroxyl ion is obtained at approximately 850 cm^{-1}.

7. A method as defined in claim 2 wherein a characteristic of a pulp or pulp effluent is determined from the relationship, said characteristic being one of pulp brightness, pulp yellowness, and bleaching efficiency.

8. A method as defined in claim 7 wherein the characteristic is related to at least one of an absorption and scattering of pulp or textiles.

9. A method as defined in claim 7 further comprising the step of adjusting an amount of peroxide for obtaining a predetermined amount of peroxide for adjusting the characteristic of the sample.

10. A method as defined in claim 2 wherein the relationship is obtained by applying regression and chemometric methods.

11. A method for determining a property of a sample comprising the steps of:

(a) irradiating at least a portion of the sample with a laser light for generating a Raman emitted light from the sample;

(b) obtaining at least two measurements of the Raman emitted light between 200 cm^{-1} and 4000 cm^{-1}, a first measurement at a first wavenumber and a second measurement at a second wavenumber; and

(c) determining a non-linear relationship between the at least two measurements and the property of the sample.

12. A method as defined in claim 11 wherein the non-linear relationship is determined by regression methods.

13. A method as defined in claim 12 wherein the non-linear relationship is expressed as at least one of the following functions between the property of the sample and the first and second measurement:

property of sample = f (first measurement, first measurement / second measurement);

5   property of sample = f (first measurement, first measurement * second measurement);

property of sample = f (first measurement, first measurement / first measurement + second measurement); and

property of sample = f (first measurement, first measurement + second measurement / first measurement).

10

14. A method as defined in claim 12 further comprising the steps of obtaining at least third measurement of the Raman emitted light between 200 cm^{-1} and 4000 cm^{-1} and determining a non-linear relationship between the at least three measurements and the property of the sample.

15

15. A method as defined in claim 14 further comprising the step of formulating at least two ratios from the at least three measurements.

16. A method as defined in claim 13 further comprising the step of controlling the
20   property in a process using feedback control for adjusting at least one feed input component in accordance with a determined value of the property for obtaining a predetermined value of the property.

17. A method as defined in claim 16 wherein the sample is produced by one of a wood
25   pulp bleaching process and a wood pulp delignification process.

18. A method as defined in claim 16 wherein the property is one of an equilibrium property, a property that occurs due to competitive processes where relative rate constants are important, and a property that signifies an extent of a reaction.

30

19. A method as defined in claim 18 wherein the property is one of pulp bleaching and pulp delignification.

20. A method as defined in claim 18 wherein the property that signifies the extent of the reaction is a degree of polymerisation.

21. A method as defined in claim 18 wherein the property is one of a degree of polymerisation, ionisation, and network formation of a silicate solution.

22. A method as defined in claim 18 wherein the property is related to an amount of organic substances in the sample, said property being one of chemical oxygen demand, biological oxygen demand, and total organic carbon.

23. A method as defined in claim 18 wherein the property is one of an amount of ionised species and a charge density.

24. A method as defined in claim 18 wherein the property is related to a propensity to form scale.

25. A method as defined in claim 18 wherein the property is an oxidation reduction potential of the sample or another measure of the oxidative or reductive capacity of the sample.

26. A method as defined in claim 18 wherein the property is a relative amount of a transient species with respect to either a reactant or a product during a chemical reaction or processing step.

27. A method for determining a potential of an oxidative reductive process comprising the following steps:

(a) irradiating at least a portion of the sample with a laser light for generating a Raman emitted light from the sample;

(b) obtaining at least two measurements of the Raman emitted light between 200 cm^{-1} and 4000 cm^{-1}, a first measurement at a first wavenumber, and a second

5   measurement at a second wavenumber; and

(c) determining a relationship between the two measurements and the potential of the oxidative reductive process.

28. A method as defined in claim 27 wherein the at least two measurements are Raman

10   intensities and wherein at least one of the intensities is an intensity peak.

29. A method as defined in claim 27 wherein the relationship includes at least a ratio based on the two measurements.

15   30. A method as defined in claim 29 wherein the relationship is derived from a Nernst equation.

31. A method as defined in claim 29 wherein the sample includes molecules with elements that exist in one of a plurality of oxidation states.

20

32. A method as defined in claim 31 wherein the elements include nitrogen, sulfur, phosphorus, chlorine, manganese, and chromium.

33. A method as defined in claim 31 wherein the molecules include sulfides, cyanides,

25   chromates, and nitrates.

34. A method as defined in claim 31 wherein the molecules are substances for one of bleaching pulp, textiles, and food substances, said molecules including sulfite, chlorine dioxide, chlorite, and hydrogen peroxide.

30

51

35. A method for measuring an amount of at least one of hydrogen peroxide and peroxyl
ion (HOO⁻) in a solution, comprising the steps of:

irradiating at least a portion of the solution with light of a suitable wavelength and
intensity to obtain information relating to a Raman spectrum thereof, said information

5   containing data related to at least one of an intensity peak corresponding to peroxide and
an intensity peak corresponding to peroxyl ion; and,

processing the information to determine indicia of a concentration of at least one
of hydrogen peroxide and peroxyl ion, the processing including an analysis of at least one
of data related to the intensity peak corresponding to peroxide, data related to the

10   intensity peak corresponding to peroxyl ion, a sum of data related to the intensity peaks
of the peroxide and peroxyl ion, a product of data related to the intensity peaks of the
peroxide and peroxyl ion, and a ratio of data related to the intensity peaks of the peroxide
and peroxyl ion.

15   36. An apparatus for determining a property of a sample comprising:

a laser light source for irradiating at least a portion of the sample for generating a
Raman emitted light from the sample;

a detector for detecting the Raman emitted light from the sample, said detector for
obtaining at least two measurements of he Raman emitted light, a first measurement at a

20   first wavenumber and a second measurement at a second wavenumber; and

a processor for receiving and processing data from the detector for determining a
non-linear relationship between the at least two measurements and the property of the
sample.

25   37. An apparatus as defined in claim 36 wherein the non-linear relationship is
determined by regression methods.

38. An apparatus as defined in claim 37 wherein the non-linear relationship is expressed
as at least one of the following functions between the property of the sample and the first

30   and second measurement:

property of sample = f (first measurement, first measurement / second measurement);

property of sample = f (first measurement, first measurement * second measurement);

property of sample = f (first measurement, first measurement / first measurement +

second measurement); and

5   property of sample = f (first measurement, first measurement + second measurement /

first measurement).

39. An apparatus as defined in claim 38 further comprising a member for controlling the

property in a process using feedback control for adjusting at least one feed input

10   component in accordance with a determined value of the property for obtaining a

predetermined value of the property.

40. A system for determining a property of a sample comprising:

means for determining a non-linear relationship between at least two measurements and

15   the property of the sample, the at least two measurements corresponding to Raman

emitted light between 200 cm^{-1} and 4000 cm^{-1}, and the at least two measurements

comprising a first measurement at a first wavenumber and a second measurement at a

second wavenumber.

20   41. A system for determining a property of a sample comprising:

means for comparing at least two measurements including a first measurement at a first

wavenumber and a second measurement at a second wavenumber, the at least two

measurements corresponding to Raman emitted light between 200 cm^{-1} and 4000 cm^{-1}

when the sample is irradiated with a laser;

25   means for determining a non-linear relationship between the at least two measurements

and the property of the sample; and,

means for determining the property of the sample in dependence upon the non-linear

relationship.

42. A system for determining an amount of at least one of hydrogen peroxide and HOO-
in a solution, comprising:

means for receiving information containing data related to at least one of a Raman
intensity peak corresponding to peroxide and a Raman intensity peak corresponding to

5   peroxyl ion; and,

means for processing the information to determine indicia of a concentration of at least
one of peroxide and peroxyl ion, the processing including an analysis of at least one of
data related to the intensity peak corresponding to peroxide, data related the intensity
peak corresponding to peroxyl ion, a sum of data related to the intensity peaks of the

10   peroxide and peroxyl ion, a product of data related to the intensity peaks of the peroxide
and peroxyl ion, and a ratio of data related to the intensity peaks of the peroxide and
peroxyl ion.

15

ABSTRACT

The invention relates to the use of ratios, products and non-linear functions of adsorption, emission or scattering of light as variables in standard regression and chemometric techniques to predict a characteristic or property of a solid or liquid. The use of one or more non-linear functions within a relationship between measured spectral properties and characteristic properties of solutions and solids provides an improved means to determine a property when the intensities represent or relate to components that are colinear or interelated due to restraints associated with composition, chemical processes, or molecular structure. The invention relates to the use of ratios of Raman peak intensities to predict the properties of a solution or a solid such as pulp that is processed with the solution. The intensity of the Raman shifted light is used to create Raman peak intensity ratios. These Raman intensities are related to the concentration of species dissolved in the liquid. The Raman spectra are baseline corrected and the scattering from a water reference is subtracted before extraction of intensities for Raman peak intensity ratios. The Raman scattering intensities provide a good measure of the concentration of small, oxygenated molecules. The potential of an oxidative reductive process is conveniently determined using Raman peak intensity ratios. Relevant small molecules and complex ions in the pulp and paper industry include SO_4^{2-}, SO_3^{2-}, H_2O_2, ClO2, $HClO_3$, silicates, acetic acid, $HClO_3$, Chlorate ClO_3^-, Chlorous Acid $HClO_2$, Chlorite ClO_2^-, Hypochlorous Acid HClO. Hypochlorite ClO^-, phosphate, nitrate, nitrites. The method may also be used to determine a property related to the relative size, degree of polymerization, branching or network formation of complexing or polymerized species. The method may also be used to measure large molecules such as hemicellulose, extractives and pectic substances.

18

18

H_2O_2

16

2 ~ PULP →

14
FEEDBACK
(ADD OR REDUCE)

BLEACHING TOWER/
CHAMBER

4

COMPUTER
12

PRESSING AND
FILITRATION

Raman
Spectrometer ~10

PULP AND EFFLUENT

6

Figure 1.

MatrixPlot

Figure 2

Matrix Plot

Figure 3.

Scatterplot

Figure 4

Matrix Plot

Figure 5

Matrix Plot

Figure 6

--□-- dispersive system (514.5 nm laser)

--●-- FT system (1064 nm laser)

Figure 7

Water Subtraction and Baseline Correction

Figure 8

Figure 9

Matrix Plot
Aspen TMP Pulp Bleaching with Hydrogen Peroxide
Pulp and Bleaching Pressate Properties

Figure 10

Figure 11

Predicted vs. Observed Values
Dependent variable: ISO BRIGHTNESS
Independent variables Raman intensities and intensity ratio

Figure 12

Figure 13

Matrix Plot Raman Intensity Ratios
HOO- and HOOH

Figure 14

Sulfur Oxianions

SO_4^{2-} SO_3^{2-} $S_2O_4^{2-}$

Figure 15

Sulfur Oxianions

SO_4^{2-} SO_3^{2-} $S_2O_4^{2-}$

Figure 16

Figure 17

Raman Spectra (S-O stretch)
Hydrosulfite Oxidation

isobestic point

0.006

0.000
950   1000   1050   1100   1150
wavenumber (cm⁻¹)

——— 0 minutes
········· 10 minutes
········· 20 minutes
– – – 30 minutes
········· 40 minutes
········· 50 minutes
——— 60 minutes
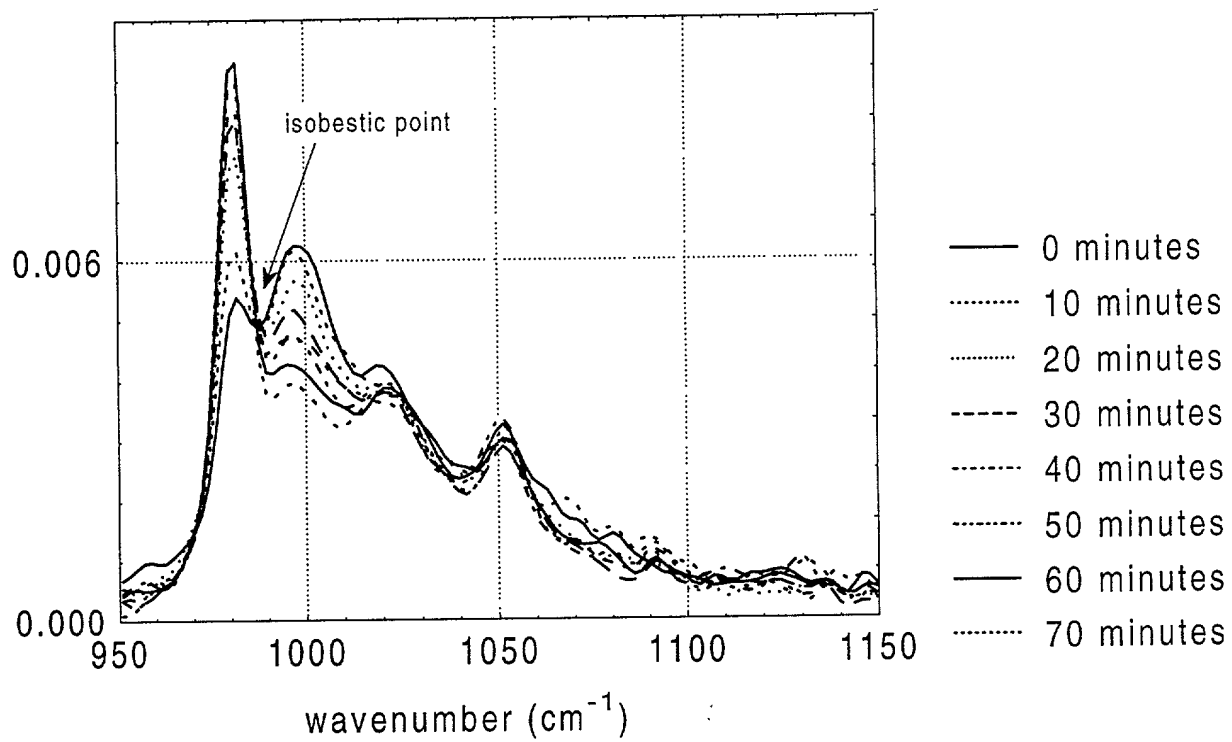········· 70 minutes

Figure 18

Matrix Plot
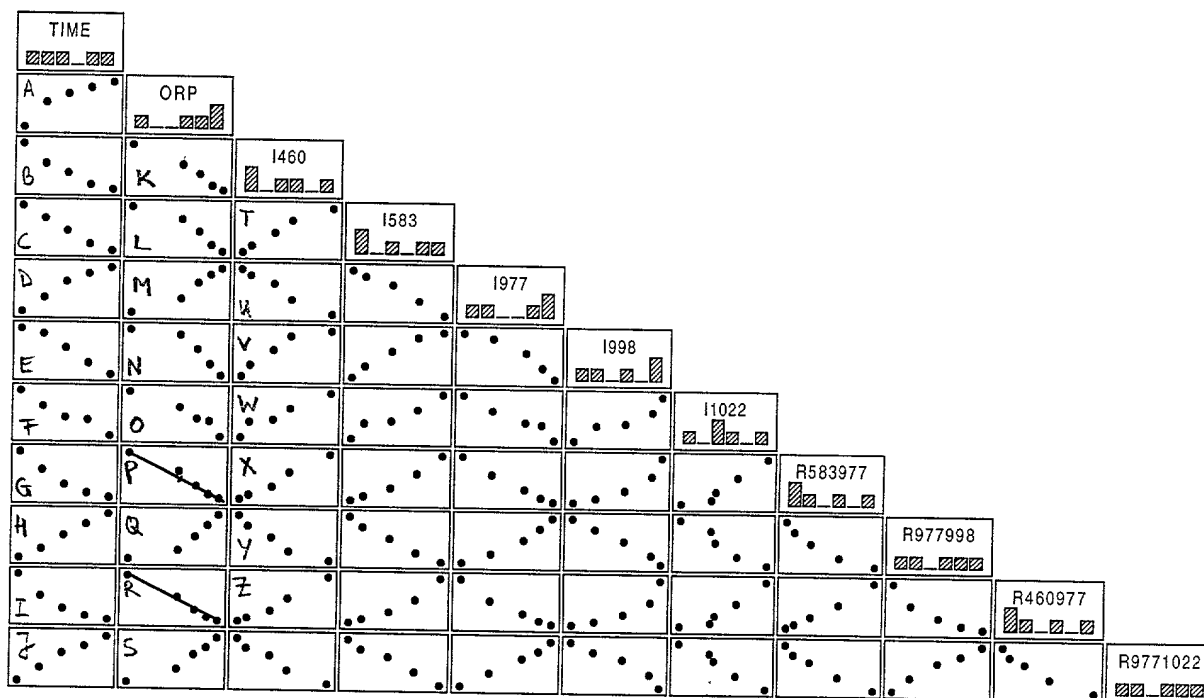## Hydrosulfite Oxidation
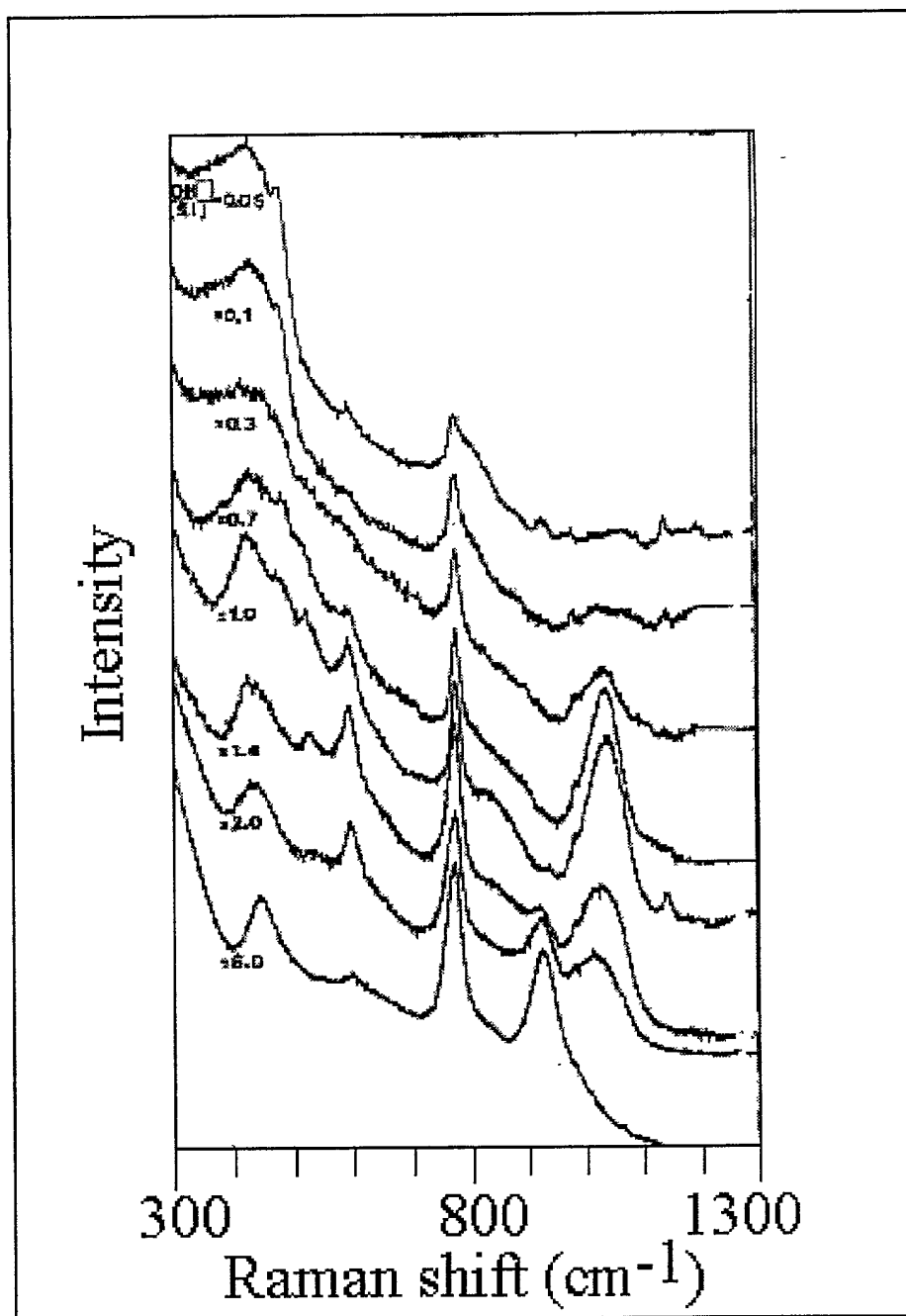## Raman Intensities and Ratios with ORP

Figure 19

Figure 20

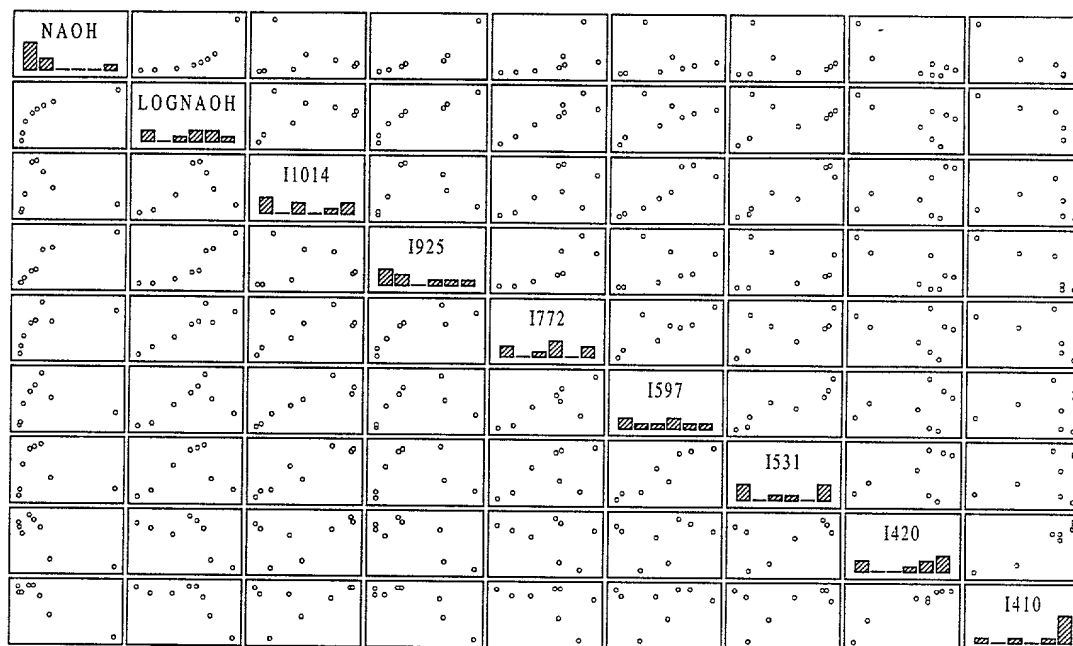Matrix Plot
Raman Data
Silicate Peak Intensities vs NaOH Added

Figure 21

Matrix Plot (Raman Peak Intensities)

Silicate Data

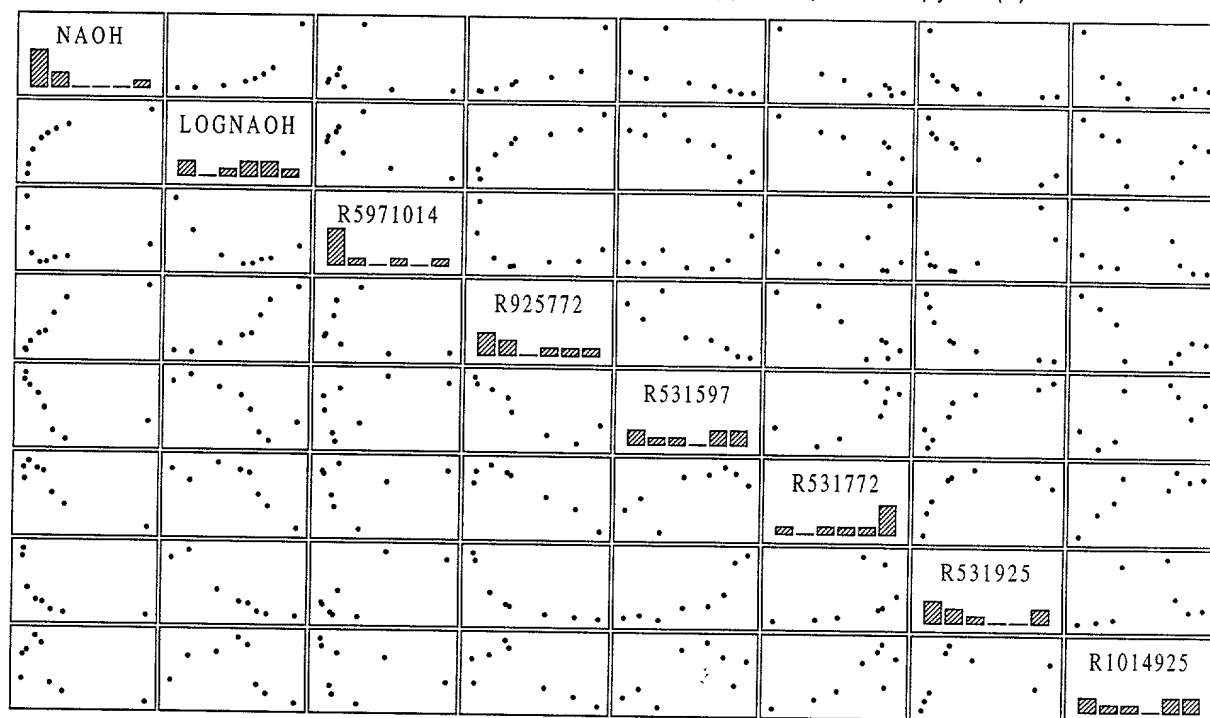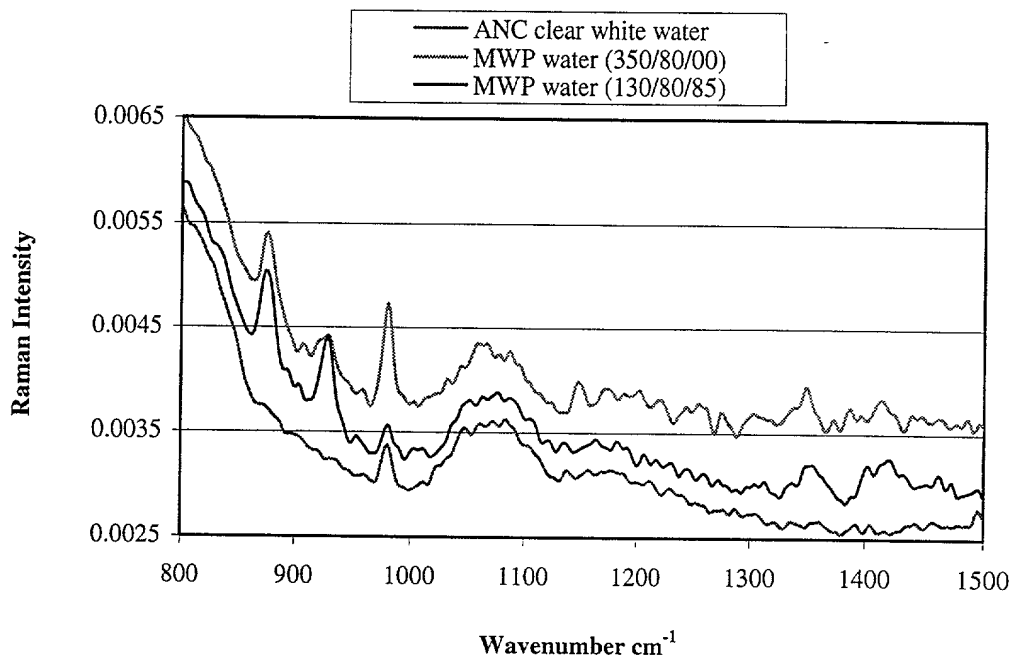Data Extracted From P.K. Dutta and D.-C. Sheih Applied Spectroscopy 39 (2) 343-6

Figure 22

Figure 23

Figure 24

File No: 51-6 US CIP

DECLARATION FOR PATENT APPLICATION

As below named inventors, we hereby declare that:

Our residence, post office addresses and citizenship are as stated below next to our names, **Theodore M. Garver and Hongqi Yuan.**

We believe we are the original, first and joint inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled

DETERMINATION OF THE PROPERTY OF A SOLUTION OR SOLID USING RAMAN RATIOS

the specification of which is attached hereto.

We hereby state that we have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

We acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of the Federal Regulations, S1.56(a).

We hereby state that this application in part discloses and claims subject matter disclosed in our earlier filed pending application Serial No: 08/814,519 filed March 10, 1997.

We hereby claim the benefit of Title 35, United States Code S119(e), of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is now disclosed in the prior United States patent application

(Number)	(Filing Date)	(Status)
		patented, pending, abandoned)
08/814,519	March 10, 1997	Pending

We hereby appoint the following agent to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Neil Teitelbaum   Regn No: 38,793
Gordon Freedman   Regn No: 41,553
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                                  Ottawa, Ontario
                                  Canada
                                  K1S 5C4

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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